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STABILITY OF COMPLEX COMPOUNDS AND EXCHANGE REACTIONS[1)]

A. A. Grinberg and L. E. Nikoskaya

In examining the experimental data on exchange we will start off by dealing briefly with the question of the stability of complex compounds, devoting our attention to the acidocomplexes which are of interest to us in this present work.

Comparison of numerous pieces of preparative work, involving mutual displacements of coordinated ions, has led to the conclusion that the different anions may be arranged in a series of increasing tendencies to complex formation with a given complex-forming substance.

Platinum for instance gives the following series:

$$CN^- > I^-,\ SCN^-,\ NO_2^- > Br^- > Cl^- > SO_4^{2-},\ NO_3^-.$$

This agrees approximately with the experimentally established order for increase of the trans-influence.

The basis for the comparison of the order of increasing tendency to complex formation is the study of equilibria of the type:

$$[MeX_4]^{2-} + 4Y^- \rightleftarrows [MeY_4]^{2-} + 4X^-.$$

The same order was obtained by one of us in collaboration with Ryabchikov [2] in the study of the equilibria of processes of the type:

$$\begin{bmatrix} OH & NH_3 \\ & Pt \\ NH_3 & OH \end{bmatrix} + 2X^- \rightleftarrows \begin{bmatrix} X & NH_3 \\ & Pt \\ NH_3 & X \end{bmatrix} + 2OH^-.$$

In this case each of the anions studied can be characterized by a definite value of the equilibrium constant:

$$K = \frac{\begin{bmatrix} X & NH_3 \\ & Pt \\ NH_3 & X \end{bmatrix} [OH^-]^2}{\begin{bmatrix} OH & NH_3 \\ & Pt \\ NH_3 & OH \end{bmatrix} [X^-]^2}.$$

Thus, with X = Cl, $K \cong 10^{-10}$., with X = SCN, $K = 2.8 \cdot 10^{-7}$;
with X = Br, $K = 2.8 \cdot 10^{-9}$., with X = I, $K = 5 \cdot 10^{-7}$.

1) See next page for footnote.

What has been said relates to the characteristic "tendency to complex formation" in aqueous solutions.

On the other hand a corresponding series of anions may be obtained by comparing the equilibrium vapor pressures in the thermal dissociation of tetrammines according to the scheme:

$$[Pt(NH_3)_4]X_2 \rightleftarrows \begin{bmatrix} X & & NH_3 \\ & Pt & \\ NH_3 & & X \end{bmatrix} + 2NH_3 [3].$$

According to the data available to us at the moment, the orders of anions according to increasing complex forming tendencies with platinum, obtained by the methods indicated, coincide (at any rate this has been established for the halide anions).

An analogous succession of anions has been found by a number of authors [4] and in the study of the molar electrical conductivity of aqueous solutions of compounds $[PtA_2X_2]$ where A = a molecule of ammonia or amine, and X = an acid radical. In the case given, chloride was found to show a much greater increase of electrical conductivity with time and a larger equilibrium value of μ, than bromide, iodide, or nitrite.

In this case the kinetic data on the rate of hydrolysis by water was found to be in agreement with the arrangement of anions, to the limits of the equilibrium attainable.

In speaking of the magnitude of the complex forming tendency, we have in mind the magnitude which characterizes the direction and degree of attainment of substitution processes, consequently, magnitudes which are thermodynamic in nature.

In solutions, this magnitude may be more strictly characterized by measuring instability constants.

To our regret the instability constants are known only for a limited number of complex compounds, obtained for extremely different complex forming substances. The values are known best of all for mercury complexes with the anions CN^-, I^-, Br^- and Cl^-.

Meanwhile, as one of us has emphasized [5] the order of anions according to tendency to complex formation with the ion Hg^{2+} agrees with the same order for platinum and palladium (and possibly also for gold).

The data given in Latimer's book permits, without any pretence to great accuracy, the evaluation of such instability constants for the anions $[PtCl_4]^{2-}$ and $[PtBr_4]^{2-}$. Knowing the value of the instability constants permits one to go a bit further in the analysis of the relationships.

Until recently the magnitude of the complex forming tendency was compared only with the properties of metal complex forming substances and anionic addends. In particular it agrees with the magnitude of the ionization potentials of metals, with the electron affinities or the polarizability of the addends, with the reducing properties of the latter, i.e. in the final analysis, with the factors determining the character and stability of the metal-addend bonds.

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1) Report presented to the session of the USSR Academy of Sciences, January 6, 1949, a brief reference to which has already been published elsewhere [1].

Kazarnovsky [7] emphasized the need to take account of the interaction of the component part of the complex with the solvent, i.e. of the energy of hydration. From his point of view, e.g., the high stability of the complex platinum iodides in solution compared with that of the chlorides is to be explained by the fact that the energy of hydration of iodide ions is less than the energy of hydration of the chloride ions.

We attempted to examine the degree of applicability of such an approximation by a method described later on.

Using the known formula: $\Delta F = -RT \ln K$, we calculated the value of the change of free energy for the mercury complex $[HgX_4]^{2-}$, for which the instability constants are known. For the calculation the following values of the constants were employed:

$$\frac{[Hg^{2+}][Cl^-]^4}{[HgCl_4^{2-}]} = 6\cdot10^{-17}; \quad \frac{[Hg^{2+}][Br^-]^4}{[HgBr_4^{2-}]} = 2.3\cdot10^{-22};$$

$$\frac{[Hg^{2+}][I^-]^4}{[HgI_4^{2-}]} = 5.3\cdot10^{-31}; \quad \frac{[Hg^{2+}][CN^-]^4}{[Hg(CN)_4^{2-}]} = 4\cdot10^{-41}.$$

By calculation from the formula $\Delta F = -1.36 \log K$ the following values of ΔF were obtained (in cal):

For chloride systems 22.1; for iodide systems 41.3;
for bromide systems 29.5; for cyanide systems 54.8.

The data for change of free energy given relates to the formation of hydrated complex ions from hydrated metal ion and hydrated anions. According to Latimer the instability constants of the anions $[PtCl_4]^{2-}$ and $[PtBr_4]^{2-}$ may be evaluated. They come out at 10^{-16} and 10^{-18}. This gives a value of ΔF equal to 21.8 cal for $[PtCl_4]^{2-}$ and 24.5 cal for $[PtBr_4]^{2-}$.

Let us divide the process of formation of hydrated complex ions from the hydrated components into the following stages:

1) dehydration of the metal ion, absorbing an energy H_{Me} per mol;
2) dehydration of 4 ions X^-, absorbing the energy of hydration H_X multiplied by 4 ($4H_X$);
3) formation of the dehydrated complex ion $[HgX_4]^{2-}$ from the dehydrated components, in which the energy A is liberated;
4) hydration of the complex ion with liberation of the energy H (complex).

All magnitudes are related to the process of the interaction of 1 mol of hydrated ion of metal with 4 mols of X^-.

Starting from this it may be assumed that

$$\Delta F = -H_{Me} - 4H_X + A + H_{complex}. \qquad (1)$$

For each separate case there are many unknowns in this expression, and they can only be evaluated extremely approximately. However, if we take the difference for two systems then the H_{Me} term disappears, and the H (complex) terms may be taken as equal (a very rough approximation) or they may be evaluated on the basis of further data.

Taking as an example iodide and chloride systems and neglecting, initially, differences in energy of hydration of the complex ions, we obtain:

$$\Delta F_I - \Delta F_{Cl} = - 4H_I + 4H_{Cl} + A_I - A_{Cl}. \quad (2)$$

Assuming a numerical value for the difference of the free energy of the whole process and also for the free energy of hydration of the iodine and chloride ions, we have

$$19.2 = (-70)\cdot 4 + (84.2)\cdot 4 + A_I - A_{Cl},$$

$$19.2 = - 280 + 336.8 + A_I - A_{Cl},$$

$$19.2 = 56.8 + A_I - A_{Cl}; \text{ whence}$$

$$A_{Cl} = A_I + 37.6 \text{ cal.}$$

Thus, by making these assumptions we come to the conclusion that change of the free energy in the formation of a mol of $[HgCl_4]^{2-}$ from the unhydrated ion Hg^{2+} and the unhydrated chloride ion is 37.6 cal larger than the corresponding magnitude for a mole of $[HgI_4]^{2-}$. Taking into account the character of the assumptions made, the important thing here of course is not the absolute value of the difference but its sign. The conclusion drawn by us would not be changed qualitatively if we were to take into account the undoubted actual inequality of the energy of hydration of the complex ions $[HgCl_4]^{2-}$ and $[HgI_4]^{2-}$. It may be assumed to a high degree of probability that the energy of hydration of the ions $[HgI_4]^{2-}$ characterized by a large radius and including components having a smaller tendency to hydration in the free state, will be less than the energy of hydration of $[HgCl_4]^{2-}$.

To evaluate this difference in energy of hydration, we may use Foit's equation, put forward for the calculation of heat of hydration of ions. For anions this equation has the form:

$$L = \frac{165.5Z^2}{r + 0.4},$$

where L is the heat of hydration of the ion, Z is its charge and r is its radius.

Calculating thus the difference of heat of hydration of the ions which interest us gives a value of 20 cal (per mol). If we assume that the difference of free energy only differs slightly from the difference in heat of hydration, then it can be concluded that the difference of free energy of hydration of free chloride and iodide ions will compensate by approximately 20 cal the difference of the corresponding magnitudes for the complex ions.

From this extremely preliminary calculation we find that $A_{Cl} - A_I \cong 17 - 18$ cal.

Thus we see that the direction of the reaction in the system $[HgCl_4]^{2-} + 4I^- \rightleftarrows [HgI_4]^{2-} + 4Cl^-$ is not in contradiction with Kazarnovsky's suggestion that the decisive factor determining the stability of the complex ion in aqueous solutions is the energy of hydration of the addend.

However, in the general case such a proposition is incorrect. This is seen quite clearly by a comparison of data for the heats of hydration of different ions, as in analysis of the system $[Hg(CN)_4]^{2-}$.

Comparison for the data for heat of hydration can be made on the basis of the papers of Yatsimirsky [9] and Mishchenko [10]; thus, e.g. according to the first author the heat of hydration of the NO_2^- ion is 100 cal while it is 84 for Cl^-. The heat of hydration of NO_3^- according to Yatsimirsky is 75 cal and according to Mishchenko it is 72 cal. On the basis of these figures it would appear that the tendency of the NO_2^- ions to complex formation would be less than that of the Cl^- ion, and the complex forming tendency of the latter would be less than that of

the NO_3^- ions. Such a conclusion would be in complete contradiction of experiment. It is impossible to make it if the composition of the cycle examined above is borne in mind. On the other hand the average value of the heat of hydration calculated by Yatsimirsky for CN^- is 85 cal. This heat of hydration of the cyanide ion is practically equal to the heat of hydration of the chloride ion. Knowing this we may, by comparison with the change of free energy for cyanide and chloride systems of the $[HgX_4]^{2-}$ type, draw the conclusion that the great stability of the cyanide system by comparison with the chloride one is conditioned by the greater stability of the Hg-CN bond by comparison with the Hg-Cl bond or, (which is less probable), by a sharp rise in the energy of hydration of the ion $[Hg(CN)_4]^{2-}$ over that of the ion $[HgCl_4]^{2-}$.

Resuming, it may be said that the energy of hydration is only one of the factors influencing the stability of complex compounds in solution, so that with a given central atom it is necessary to take into account both the energy of hydration of the addend as well as the energy of hydration of the complex ions.

A decisive influence on the direction of the process of substitution of addends towards the formation of a more stable system can be exerted by the energy of hydration of the addend only in those cases, where the difference of the relevant magnitude for the initial and final addend is large and only to a small degree compensated by the difference of energy of hydration of the initial and final complex ions.

As we saw in such cases the quantity determining the stability of the system is the change of free energy in the formation of the complex ion from the dehydrated central ion and the unhydrated ions. It should be noted that this change includes a portion connected with the approximation of the Me-X bond to the covalent type.

In the case given the central ion and the coordinated anion are to be thought of initially as typically gaseous ions. As one ion approaches the other oxidative-reductive interaction occurs which approximates the system to a covalent bond. There is no doubt that the diminution of the electron affinity of the anion, other conditions being the same, increases the degree of "covalentness" of the bond. Therefore, for example, the bond Hg-I or Pt-I is more covalent than the Hg-Cl or the Pt-Cl one. But the bond Me-X, generally speaking, may be broken by two methods:

$$Me - X \rightleftarrows Me^0 + X^0 \quad \text{and} \quad Me - X \rightleftarrows Me^+ + X^-.$$

Increasing the degree of covalentness of the bond favors the breakdown to the first type and lowers the probability of breakdown to the second. In complete agreement with this, as earlier published by one of us, [11], $[PtCl_6]^{2-}$ breaks down more readily to $[PtI_4]^{2-}$ and I_2 than $[PtCl_6]^{2-}$ to $[PtCl_4]^{2-}$ and Cl_2. However, an inverted relationship may attach to the concept of ease of breakdown to ions. It cannot be doubted that the degree of covalentness of the bond Me-addend is considerable and that the complex ion has a definite stability in solution.

It is likewise quite evident that calculation of this factor is completely tied up with the general thermodynamic treatment of the question.

The calculations set forth and the discussions relate mainly to mercury complexes. However, the facts of the agreement of the order of stability and the order of magnitude of the instability constants makes it highly probable that the same characteristic relationship holds for platinum as well.

Before we conclude this section we should like to dwell briefly on a couple of points.

First, we should like to underline the need for systematic study of the stepwise dissociation of complex compounds. In this direction there is a very interesting investigation by Babko [12], applicable to some acidocomplexes, and of Bjerrum [13], applicable to amine and ammine complexes, but both urgently requiring further investigation.

On the basis of the data at our disposal it can be said that in the majority of known cases the stepwise dissociation of complex ions follows the same rule as that of monobasic acids. In particular usually the fission of each successive ion X- from ions of the type $[MeX_4]^{2-}$ is more difficult than the fission of the first. There are individual deviations from this rule. The question urgently requires further study.

The relationships are very interesting in the case of the ion $[HgCl_4]^{2-}$. As mentioned above constants are known for this ion corresponding to the process $[HgCl_4]^{2-} \rightleftarrows HgCl_2 + 2Cl^-$, and likewise "overall" constants. If we designate the constants corresponding to the separate dissociation stages by K_1, K_2, K_3, K_4, then the overall constants $K = K_1 \cdot K_2 \cdot K_3 \cdot K_4$.

The constants corresponding to the process $[HgCl_4]^{2-} \rightleftarrows HgCl_2 + 2Cl^-$, $K' = K_1 \cdot K_2 = 1.10^{-2}$, while $K = K_1 \cdot K_2 \cdot K_3 \cdot K_4 = 6.10^{-17}$.

In the same way $K_3 \cdot K_4 = 6.10^{-15}$, i.e. there is a very sharp difference in the ease of separation of the last two anions by comparison with the first two. At first sight this might be explained as a difference in behavior of anions found by main and subsidiary valencies.

However, according to Bjerrum's data, completely analogous differences of the first and second pairs of successive constants are observed in cases of tetrammine ions, in which all addends are bound by subsidiary valencies. The "overall" constant K for $[Hg(NH_3)_4]^{2+}$ is equal to $5.2 \cdot 10^{-20}$; $K_1 = 1.1 \cdot 10^{-1}$; $K_2 = 1.5 \cdot 10^{-1}$; $K_3 = 2 \cdot 10^{-9}$; $K_4 = 1.6 \cdot 10^{-9}$.

Similar phenomena which occur with monobasic acids (for example with pyrophosphoric acid) are probably connected with some peculiarity of the structures of the corresponding compounds.

In the case of mercury compounds it may be supposed that such sharp differences in the K_4, K_3, K_2 and K_1 values are connected with a transition from a linear structure of the ion with two addends to a tetrahedral structure of the anions with four addends. The final solution of such questions requires further investigation.

Naturally, the difference of constants of the stepwise dissociation by themselves cannot in any way serve as indexes of functional inequalities of groups in undissociated compounds. An interesting fact which is in agreement with this view (about non-equivalence) is that Wells [14] in his book "Structural Inorganic Chemistry" makes the following statement about crystals of $K_2HgCl_4 \cdot H_2O$: "The atom of mercury has two neighbouring chlorine atoms which are considerably nearer to one another than the other atoms."

From the literature interesting data may be extracted relative to the dissociation constants for the processes: $[Hg(CN)_4]^{--} \rightleftarrows [Hg(CN)_3]^- + CN^-$ and $[Zn(CN)_4]^{--} \rightleftarrows [Zn(CN)_3]^- + CN^-$, which are respectively equal to 10^{-3} and $10^{-2.7}$, while the overall constants are equal to $4\ 10^{-42}$ and $10^{-16.9}$.

The second point on which we wish to dwell is connected with the question of the energetics of complexes in solutions.

In order for the complex or weak electrolyte dissolved in water to remain undecomposed (undissociated) it is necessary that it should not rearrange during the continuous collisions with molecules of the solvent. In other words this means that the free energy of formation of the corresponding forms should considerably exceed the average kinetic energy of the molecule at the given temperature, i.e. should exceed $1\frac{1}{2}$ RT.

In [1], using the relationship $-\Delta F = RT \ln K = -1.36 \log K$, we came to the conclusion that there should be an upper limit for the dissociation constant expressed by the formula $K = \frac{\alpha^2 C}{1-\alpha}$ ($K = 0.22$).

In other words this would be a magnitude of the degree of dissociation of the electrolyte, on exceeding which during the process of dissociation the law of mass action would become inapplicable, unless corrected for interionic attractions.

It is possible (this needs further proof) that the conception of a "heat" threshold may be compared with "limits" separating the fields of "weak" and "strong" electrolytes. This delineation naturally is not absolutely rigid and is justified to the extent to which it applies for the conception of "strong" and "weak" electrolytes.

Let us turn our attention to data about exchange reactions of addends and complexes. Investigations in this direction, using tagged atoms, were carried out by us, starting in 1939.

In that year it was shown that the complex bromides of di- and tetravalent platinum fairly easily exchange co-ordinated bromine for ionic bromine in the ambient solution [15].

This fact, interesting in itself, was utilized by us as an index of the equivalence of bonds in the $[PtBr_4]^{2-}$ ion and of the equivalence of the co-ordinate bonds in the ion $[PtBr_6]^{2-}$. Analagous data for the ion $[HgI_4]^{2-}$ were easily obtained by Polesitski [16]. The occurence of rapid exchange was recorded not only for acidocomplexes but also for the case of cis-$[Pt(NH_3)_2Br_2]$ where the factor of labilization of the opposed transactive residue is excluded [17].

Later on, by using tagged platinum atoms, we were able to discover oxidative reductive exchange, expressed for example in the fact that the ions $[PtX_4]^{2-}$ and $[PtX_6]^{2-}$, changed their role in solution, and likewise (for example in the platinic as in the iridous complexes) the absence of exchange with central ions characteristic for stable complexes. Together with this it was also observed that exchange with central ions is not always absent. In particular such exchange was found for example in the systems $CuGl_2$ (Gl = NH_2CH_2COO) and $CuSO_4$, using labelled atoms of copper [18]. In connection with these phenomena we have suggested that the absence of rapid exchange of central ions of complexes with the corresponding free ions in solution, is a manifestation of the need to maintain a definite spatial configuration in solution. The presence or absence of such exchange may serve as a criterion of the expediency of looking for corresponding (geometric or optical) isomers.

Among the foreign contributions in this field the works of Kennedy, Ruben and Siborg [19] should be mentioned. They demonstrated the absence of exchange of ions between $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ and likewise between Fe^{3+} ions and $[Fe(CN)_6]^{3-}$. Ruben, Kamen and Frenkel [20] tried in vain to observe exchange between Mg^{2+} and chlorophyll, and likewise between Fe^{3+} and hemoglobin.

Apart from this, attempts have been made to observe exchange between ions of Co^{2+} and complex cobaltiammine ions [21]. These experiments likewise did not have a positive outcome. Calvin and his collaborators studied the exchange between Cu^{2+} ions and internally complex compounds of copper [22]. This investigation was development of the work mentioned above, completed in our laboratory, although the authors do not mention the fact. Ettle and Johnson [23] used tagged chlorine to elucidate the mechanism of rearrangement of dichlordiethylendiamine compounds of cobalt.

There is a very interesting paper by Long [24] beginning with a study of the exchange between $C_2O_4^{2-}$ and $[Cr(C_2O_4)_3]^{3-}$ in order to elucidate the mechanism of racemization; no exchange was observed. Later he studied the complete family of trioxalates and showed that cobalt and chromium trioxalate did not show any exchange, but derivatives of aluminum and iron showed a rapid exchange. The author connected the results with the fact that in cobalt and chromium complexes there are covalent bonds, while in the derivatives of Al and Fe there are ionic ones. Thus Long studied the behavior of groups of compounds with identical addends but difference central ions.

EXPERIMENTAL

In our work we decided to study the behavior of acidocomplexes of the type $K_2[PtX_4]$ differing in the nature of the co-ordinated groups. In particular, in our experiments X represented Cl^-, Br^-, I^-, CN^-. At the same time we also studied the systems $K_4[Fe(CN)_6] + C\bar{N}^-$. Since it was not necessary for us to separate the tagged X^- from the basic mass of X^-, in distinction from the procedure used in previous work, namely the method of Szillard and Chalmers, the tagged atoms of halogen were prepared by irradiating NH_4X salts where X = Cl,Br,I. In this way $Cl^{(38)}$, a mixture of $Br^{(80)}$ and $Br^{(82)}$, and $I^{(128)}$ was obtained. Under the conditions of reaction practically only the halogen was activated in the compound NH_4X.

Only be means of the above mentioned method was the performance of the experiment with halogenides very much simplified. Attempting to snythesize cyanide derivatives by the simplest possible means we started out from the assumption that the nitrogen atoms formed in the corresponding nuclear reactions should be chemically very active and ought to interact with carbon forming $C\bar{N}$. If this were correct then it would be expected that CN could be got into solution by shaking irradiated carbon plates with a solution of ordinary KCN. Experiment completely confirmed our expectations. To confirm that we actually had obtained active cyanide, we carried out a whole series of control experiments.

Thus, for example, we distilled HCN from a solution acidified with H_2SO_4, mixed the distillate with a solution of KCN and confirmed the activity by precipitation of silver cyanide and measurement of the decay period of the active preparation.

By such experiments we were able to make certain that we had actually synthesized cyanide containing active nitrogen as a result of a nuclear reaction. This is an interesting example of a "nuclear" chemical synthesis by a nuclear reaction.

In this way active halogen and cyanide ions were prepared and were used for the study of exchange with compounds of the $K_2[PtX_4]$ type. Active cyanide ions were also used for studying the exchange of cyanide with $K_4[Fe(CN)_6]$.

Such exchange experiments were carried out as follows: A definite weight of the salts $K_2[PtX_4]$ was taken, dissolved in water and to the solution an aliquot

weighed quantity of solution of the irradiated preparation NH_4X was added in such quantity that the equilibrium distribution of activity between the complex ion $[PtX_4]^{2-}$ and the free ions X^- was quite definite (for example 50%). Such a distribution could be obtained if the weight of ions X^- in the complex is equal to the weight of ions X^- outside the complex. The solution was shaken for some time at a definite temperature. To terminate the exchange an excess of reagent was added to the solution, precipitating the complex ion $[PtX_4]^{2-}$ and preventing the exchange interaction with the X^- ions. In working with the complex ions $[PtX_4]^{2-}$ (X = Cl, Br, I) a tetrammine-plato-chloride $[Pt(NH_3)_4]Cl_2$ was used as a precipitating reagent. In the case of $K_2[Pt(CN)_4]$ precipitation was made with benzidine hydrochloride because the compound $[Pt(NH_3)_4]Cl_2$ under the conditions of the experiment, reacts with KCN with elimination of NH_3 and formation of the ion $[Pt(CN)_4]^{2-}$.

Special experiments were carried out to establish that benzidine hydrochloride reacts with $K_2[Pt(CN)_4]$ with formation of the low solubility compound $(C_6H_4NH_3)_2[Pt(CN)_4]$, the composition of which was found by analysis to be: Pt Calculated %: 40.21. Found %: 40.60, 40.10, 39.4; average 40.03.

The precipitate obtained after washing the water, alcohol, and ether was wrapped in cellophane and subjected to measurement. For comparison the activity "titer" of a precipitate of silver salt AgX, was measured, this having been precipated from another, similar, aliquot of the test solution of the weighed irradiated preparation. In working with $K_4[Fe(CN)_6]$ we used another precipitant for the complex ion, this being lead nitrate after acidification of the solution of the complex), benzidine hydrochloride and calcium nitrate in the presence of ammonium ions.

TABLE 1

Exchange with different platinic systems

Duration of exchange (min)	Theoretically calculated percentage equilibrium activity in the complex for complete exchange	Percent activity in the complex found by experiment	Degree of exchange (in %)
	System $[Pt(CN)]_4^{2-} + CN^-$		
1	47	27	57
1	54	32	59
1	61	36	60
5	54	52	95
5	54	45	83
	System $[PtCl_4]^{2-} + Cl^-$		
20	50	No Activity	No Exchange
35	75	ditto	ditto
60	51	6	11
	System $[PtBr_4]^{2-} + Br^-$		
40	31.5	31	100
20	31	18	58
25	40	26	65
25	40	28	70
	System $[PtI_4]^{2-} + I^-$		
10	50	31	62
25	39	36	92
25	42	42	100

The results obtained, collected in Tables 1 and 2, show that exchange occurs in all the platinic systems studied. The rate of exchange depends in a definite way on the nature of the co-ordinated group. The equilibrium activity distribution was obtained more rapidly in the case of the $[Pt(CN)_4]^{2-}$ ions. After this, in descending order are the ions and $[PtI_4]^{2-}$, $[PtBr_4]^{2-}$, and $[PtCl_4]^{2-}$. No exchange occurred with yellow potassium ferricyanide.

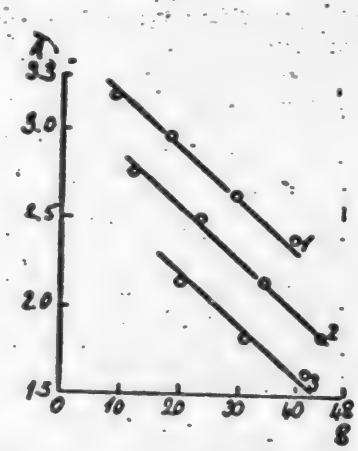
We shall dwell initially on platinum compounds. The data obtained by us indicate the rate of exchange between complex ions and the corresponding free ions in solution. Thus, these data are in essence kinetic. Kinetic data are not always simply related to thermodynamic magnitudes which characterize the stability of a system.

But in the case given we observed a very interesting relationship determined apparently by characteristic peculiarities of the systems studied.

TABLE 2

Comparison of rates of exchange in the system $[PtX_4]^{2-} + X^{*-}$ as a function of the nature of the co-ordinated anion.

Anion	Time of attainment of equilibrium activity distribution (in minutes).
CN^-	5
I^-	25
Br^-	40
Cl^-	60[1]



Exchange of ions of cyanide with $K_2Pt(CN)_4$.
A) log N; B) time (in minutes); 1) activity "titer"; 2) activity of complex by direct exchange; 3) activity of complex by "reverse exchange".

We can see that the more stable the system in the thermodynamic sense the more rapid the exchange. At a first glance this appears to be a paradox. However, it may be understood if it is considered that in all cases known to us the cyanide ion is very easily and rapidly replaced by other groups co-ordinated with the divalent platinum ion. Thus, for example, cyanide ions displaced chlorine ions with extreme ease from $[PtCl_4]^{2-}$, molecules of NH_3 from the $[Pt(NH_3)_4]^{2-}$, dimethylglyoxime residues from a molecule of PtD_2H_2, etc. Second place is taken by the iodide ion, thereafter comes the bromide ion and finally the kinetically most sluggish chlorine ion. Thus, the anions studied by us are arranged in the same order according to the ease of their introduction into the complex ion of divalent platinum with different co-ordinated addends, in general by the facility of replacement of the given ion, this order being the same as that of its stability and the rate of the exchange we studied. We can conclude that the CN ion can most readily displace other groups co-ordinated to platinum, extending this ability so far that it is " self-replacing".

However, the practically complete absence of exchange with ferrocyanide ions shows that the cyanide ion does not always behave in this way. It is evident that there is a great difference between the platinocyanide and the ferrocyanide ions.

Although we have no accurate data relative to the instability constants of the platinocyanide ion, nevertheless on the basis of the order of placing of the

[1]) Exchange occurred only to the extent of 11% in one hour.

ions it can be asserted with complete certainty that the platinocyanide ion in the given case is no less stable than the ferrocyanide ion, but the former differs from the latter in its co-ordination type, in its charge, and in the size of the trans-influence group, which in the case of platinum is expressed more strongly than in the case of the derivatives of iron. The difference of the co-ordination types may be very important because compounds with co-ordination number 4 are potentially unsaturated in distinction from compounds with co-ordination number 6. In spite of everything this factor can hardly have a decisive importance in all cases. This is clear by comparison of the rate of exchange of $[Pt(CN)_4]^{2-}$ and $[PtCl_4]^{2-}$ and likewise by the existence of exchange with ions of octahedral structure $[PtX_6]^{2-}$.

The difference of charge of complex ions may and should be reflected unconditionally in the kinetics of exchange but it is doubtful whether this one circumstance can cause so large a difference in the behavior of $[Pt(CN)_4]^{2-}$ and $[Fe(CN)_6]^{4-}$. The magnitude of the trans-influence in complexes of platinum and iron is extremely different, and in our opinion it can play a considerable role in explaining the observed differences in their behavior.

Further investigation is already under way to make more precise the role of separate factors mentioned on the rate of exchange.

It is likewise not yet possible to decide finally whether exchange occurs in compounds of the $[PtX_4]^{2-}$ type by direct first degree dissociation according to the scheme: $[PtX_4]^{2-} + H_2O \rightleftarrows [PtX_3H_2O]^{-} + X^{-}$, or whether it occurs through intermediate addition of another addend according to the scheme:

$$[PtX_4]^{2-} + X^{-} \rightleftarrows [PtX_5]^{3-} \text{ and } [PtX_5]^{3-} \rightleftarrows [PtX_4]^{2-} + X^{-}.$$

All the same it is the extremely interesting fact that complexes such as $[Pt(CN)_4]^{2-}$ and $[Fe(CN)_6]^{4-}$, which are so stable in the thermodynamic sense, may yet differ so strongly from one another in the " lifetime" of the Me-CN bond.

The existence of extremely rapid exchange with $[Pt(CN)_4]^{2-}$ and the practically complete absence of exchange with $[Fe(CN)_6]^{2-}$ was established by us by a whole series of control experiments. One of these experiments was the reversal of the activity from the activated $[Pt(CN)_4]^{2-}$, by adding an excess of KCN to the solution, with a complete change of distribution. This experiment showed that reverse exchange in $[Pt(CN)_4]^{2-}$ is likewise very rapid and leads to an equilibrium distribution of activity.

The results of these experiments are shown in the figure adjoined.

The data of the experiments which we carried out to evaluate the energy of activation of the reaction $[PtCl_4]^{2-} + Cl^{-}$ and $[PtI_4]^{2-} + I^{-}$ will be presented in another paper.

Nevertheless it may be said at once that the energy of activation in the case of iodine systems is considerably less than is the energy of activation in the case of chlorine ones.

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STATE AND PROPERTIES OF SILICA IN SILICATE GLASSES [1]

A.A.Appen

The establishment of a connnection between the properties of glass and its composition is a fundamental problem in the science of glass. The prediction of the property of a glass from its chemical composition, or inversely the accurate compounding of a glass so as to have specified properties, is in principle a very important task, the solution of which is of great consequence.

The solution of this problem in its entirety is impossible without establishing a general relationship between the change of properties of glass and its composition and without careful study of the structure of glass.

A single direct method of structural analysis (X-ray and electronography) is insufficient to elucidate the structure of a glass. This is particularly true when dealing with complicated multi-component glasses. It is necessary to resort to physico-chemical investigation in all its many forms.

The methods of physico-chemical analysis used in the investigation of alloys, solutions, and molten salts (Kurnakov's school) have led, as it is known, to extremely fruitful results. These same methods are becoming more and more important in the study of glassy systems. Nevertheless, up to the present it has not been possible to find any generalized rule relating the change of the properties of a glass to its composition. Previous proposals about the applicability of the additivity rule to glass systems in general have been shown to be invalid on experiment. The deviations from the additivity rule observed in the properties of glasses by the majority of investigators have been explained by the formation of definite chemical compounds between oxides. However, attempts to establish a connection between the composition diagram and the properties of glasses, even in the simplest systems, undertaken by Evstropev [1], Kumanin [2] and other investigators have not yielded concordant results. This demonstrates the difficulty of studying glass systems. The many sided investigations or the properties of the ternary system Na_2O-PbO-SiO_2 undertaken by collective authors under the leadership of Grebenshchikov [3] showed that there is a connection between the composition diagram and the properties of these systems, in the glass form; however, it is manifested rather weakly and not in all properties and only at definite temperatures The task of establishing a connection between the properties and composition of glass becomes peculiarly difficult in the investigation of multicomponent systems, such as technical glass.

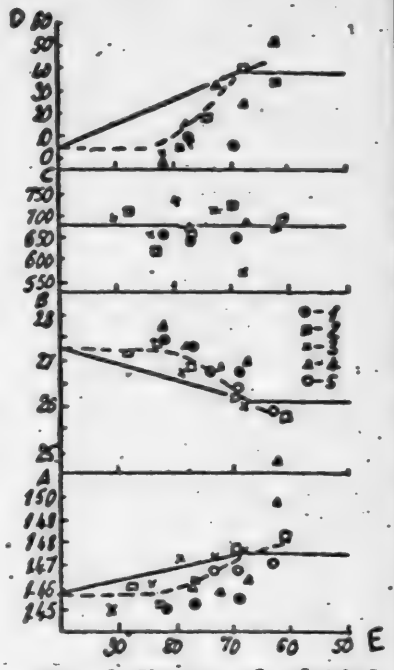

Fig. 1 Change of partial properties of silica in silicate glasses. A-$\bar{N}_{SiO_2}$; B-$\bar{V}_{SiO_2}$; C-$\bar{D}_{SiO_2}$ $\cdot 10^5$; D-α_{SiO_2} $\cdot 10^7$; molar % SiO_2. 1-Li_2O - SiO_2; 2-Na_2O-SiO_2; 3-K_2O-SiO_2; 4-Na_2O-BaO-SiO_2; 5-Na_2O-CaO-SiO_2.

The usual method of constructing the property/composition diagram, in which one of the separately measured properties of the composition, taken as a whole, is plotted on a diagram, is insufficient to treat the whole complex of phenomena occurring in complex systems. It seems desirable to look for other means of investigation. It is interesting to analyze in every given case the change of properties not in the system taken as a whole, but the change in property of separate components entering into the system. We may have confidence that such a method of analysis of the composition/property diagram will make it possible to find a general connection between the behavior of components in glasses and to obtain in some cases new, indirect, information about their molecular state.

1) See next page for footnote.

The question arises as to what part of the glass should be taken as a component, and in what units the composition of the glass should be expressed.

Thus far, attempts to study the properties of elementary ions or to suggest definite chemical compounds in glass have not had a pronounced success.

Evstropev [4], studying the change of specific volume and refraction of the oxygen ions in a glass, did not succeed in finding any unified equation relating the indicated properties of the oxygen ions with the composition of the glass. For each glass system the change in properties of the oxygen ions follows its own law and the task of generalizing the experimental material, apparently, was inconclusive.

The method of expressing the composition of glass in elementary ions (atoms) likewise has other deficiencies. In distinction from metallic alloys, in glasses it is not possible to have a quantitative relationship between atoms. The number of atoms of oxygen in the glass is not an independent variable parameter. In glass it is possible to have any relation between oxides, but not between ions. For example in the expression $xNa_2O \cdot yCaO \cdot zSiO_2$, the co-efficients x, y, z may have any value within known limits. In the expression $Na_xCa_ySi_zO_k$ the values of the co-efficients x, y, z, k must be limited by the fact that the sum of the positive valences must equal the sum of the negative valences. This method of expressing the composition of the complex system in elementary atoms seems to be fundamental in application to metallic alloys but cannot be considered suitable for application to glasses, because of the overshadowing effect of the difference between alloys and glasses referred to above.

Painstaking work in calculating the gross composition of glasses in terms of oxides of definite chemical compounds, known in the crystalline state, likewise has not proved itself of value, either from the point of view of meeting practical needs (work of Biltz and of his collaborators [5]) or from the purely theoretical point of view. The expression of the composition of a glass in terms of chemical compounds, has no particular significance, since the real composition of the chemical compounds in glasses cannot be considered to be known. It is not sufficient as a basis to assume that glass systems are composed of the same compounds as are crystalline silicates. In the glass state conditions are created which are more favorable to the existence of different undetermined chemical compounds of variable composition. The varying capacity of silica for the formation of indeterminate chemical compounds with metal oxides was particularly emphasized by Mendeleev. In his classic work " Basis of Chemistry" he wrote: " If we designate oxides by MO, then the composition of different silica compounds will be $mMO \cdot nSiO_2$".[2] Mendeleev considered glass as an amorphous melt of undetermined siliceous compounds. He considered definite chemical compounds only as limited forms of indefinite compounds. This proposal of Mendeleev's further developed by Akad. Kurnakov, should be considered a guiding principle in the interpretation of the nature and crystal structure and in particular of the glassy form of silicates.

In our work we expressed the composition of a glass in mol. fractions, mol. percentages or in number of mols of oxide. This method of expressing the composition of a glass has a definite superiority over other known methods including the following:

1) The main characteristic type of crystal structure in glassy silicates appears to be a relation of the number of atoms of silicon to the number of atoms

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[1]) Communication I on the investigation of the relation between properties and composition of glasses.

[2]) D.I. Mendeleev, Collected Works, XIV, 1736, 1949.

of oxygen $f_{Si} = \frac{n_{Si}}{n_O}$, so that the magnitude f_{Si} expresses the degree of binding of the silicon-oxygen skeleton. This f_{Si} ratio lies at the root of all contemporary classification of silicates according to their structure. To a first approximation it may be taken that glasses having identical f_{Si} values are structurally equivalent.

In Table 1 are shown as an example five methods of expressing the composition of a glass in molar or atomic ratios.

TABLE 1

Method of expressing the Composition of a Glass in Molecular Ratios

Expt No.	Method of expressing composition of the glass	Numbers characterizing the state of the glass. Glass A: $Na_2O \cdot 2SiO_2$, $f_{Si} = 0.40$	Glass B: $BaO \cdot 2SiO_2$, $f_{Si} = 0.40$
1	In oxides	Na_2O —1 SiO_2 —2	BaO—1 SiO_2—2
2	In hypothetical chemical compounds	$Na_2Si_2O_5$—1	$BaSiC_3$—1 SiO_2—1
3	In elementary cations	Na—2 Si—2	Ba—1 Si—2
4	In elementary cations and anions	Na—2 Si—2 O —5	Ba—1 Si—2 O —5
5	In the relative cation fractions	f_{Na}— $\frac{2}{5}$ f_{Si}— $\frac{2}{5}$	f_{Ba} — $\frac{1}{5}$ f_{Si} — $\frac{2}{5}$

It is evident that the composition of two glasses A and B having equal f_{Si} coefficients is expressed by the same number only in Method 1.

Thus the structural equivalent agrees with the arithmetical equivalent only in the case where the composition of the glass is expressed in oxides (in molar ratios). Such a conclusion is correct also for complicated glasses. Only the introduction into the glass of the oxides of trivalent elements (Al_2O_3, B_2O_3) introduces a change in this simple rule. Consequently it may be expected that, by expressing the composition of glass in mols of oxides, a simpler form of interconnection between the composition of the glass and its properties should be found. Our investigation completely confirmed this proposition.

2) Identical molar percentages of SiO_2 in different glasses manifest themselves also by identical average degrees coherence of the silicon oxygen skeleton. But the properties of silicate glasses depend to a considerable extent on the degree of coherence of the silicon oxygen skeleton. This factor can be most simply studied only by expressing the composition of the glass in oxides and not by other means.

3) The method of expressing the composition of a glass in oxides is more convenient in practice. It cannot be considered that this method is essentially out-of-date. Silicates are compounds intermediate in character between typical salts and oxides. Among all the salts of hydroxy acids silicates most closely approximate in their structure to ionic oxides, having a coordinate lattice. Consequently the expression of the composition of silicates in oxides does not

contradict the current state of silicate science. It is only necessary to bear in mind that by the concept of oxides in silicates is understood not discrete molecules (such do not occur in pure silicate - forming oxides either) but an association of oxygen and electropositive elementary ions in definite quantitative ratios and distributed vis-a-vis one another according to co-ordination principles.

4) In expressing the composition of a glass in oxides it is possible to equalize directly the properties of the oxide in the free crystalline and the glassy form with the properties of the same oxide in complex glasses. But on changing the properties it is possible to assess also those structural changes which oxides suffer on introducing them as component parts into complex glasses. Study of the properties of a glass should not be limited to one selected system. It is extremely important to trace the behavior of one and the same oxide in different simple and complex systems and in technical glasses. The behavior of oxides in glass should likewise be investigated not for one but for a number of properties, collecting the largest possible amount of experimental material.

We have published a number of papers on such series of investigations. In our work we used data published at home and abroad relative to properties of 40 binary, ternary and multicomponent silicate glass systems and some of our own experimental data as well. Our investigation covered in its first stage four properties of glasses: the density d or molecular volume V[1], the refraction index n_D, the mean dispersion $n_F - n_C$ and the mean coefficient of linear expansion $\alpha_{20-400°}$.

From these properties, which were examined by us simultaneously, it is possible to make a more versatile investigation into the behavior of oxides in glass.

EXPERIMENTAL

Method of determining the properties of oxides in glass. If a glass were a physical mixture of the initial oxides, the properties of the latter would remain constant in all glasses and equal or nearly equal to the property of the pure glassy or crystalline oxide. In actual fact this is never observed.

In the process of compounding a glass the initial oxides, forming in the glass, react with one another and change their state. Hence the properties of the free oxides are not equal to the properties of the oxides in the glass. The properties of the oxides in the glass may be expressed by definite numerical characteristics which, in a series of cases, may be found by simple calculation from experimental data. The method for determining the properties of the oxides in glass is deduced as follows.[2]

Let the property of interest to us be some intensive property g. The intensive properties are determined by the composition of the system but not by the quantity of material in it. We may introduce some extensive property G

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1) The molecular volume of a glass is calculated from the relations $V = \frac{\Sigma M_i \gamma_i}{d}$, where M = molecular weight of the oxides, γ_i = content of oxides in the glass in mol. fraction.

2) The deduction of the thermodynamic relationships given below was accomplished with the active participation of V.A.Kozheurov.

determined by the equation:

$$G = g(a_1 + a_2 + \ldots) = g\Sigma a_i, \qquad (1)$$

where: a_1, a_2 ... = no. of mols of components of the system; Σa_i = total no. of mols of all components of the system.

Equation (1) is correct inasfar as the extensive property of the system is determined by the quantity of each of the component parts.

On the other hand, for a characteristic extensive property of the solution the following equation is deduced in thermodynamics:

$$G = a_1\bar{g}_1 + a_2\bar{g}_2 + \ldots = \Sigma a_i\bar{g}_i, \qquad (2)$$

where $\bar{g}_i$= general representation for the quantities $\bar{g}_1$, $\bar{g}_2$, etc; the latter are partial molar quantities of the components and are determined by the relations:

$$\bar{g}_1 = \frac{\partial G}{\partial a_1}; \quad \bar{g}_2 = \frac{\partial G}{\partial a_2}, \text{ etc.} \qquad (3)$$

Solving for g with the help of Equation (1) we obtain:

$$g = \frac{\Sigma a_i\bar{g}_i}{\Sigma a_i} = \Sigma \gamma_i\bar{g}_i, \qquad (4)$$

where γ_i = general representation of mol. fractions of components γ_1, γ_2, etc.

Determining the magnitude $\bar{g}_i$ by Relation (3) we avoid the arbitary and many-valued solutions of Equations of type (4). The numerical value $\bar{g}_i$ may be found experimentally by determing the change in properties of the given system as a result of the introduction of the components under investigation.

Let us solve this problem for the general case, i.e. for a multicomponent system.

We have: $\gamma_1 + \gamma_2 + \ldots + \gamma_k = 1$.

Let the mol. fractions of the first component change by some amount while the ratio of all other components one to another remains constant. The magnitude g may in this case be considered as a function only of γ_1. Consequently we shall have:

$$G = g\Sigma a_i;$$

$$\bar{g}_1 = \frac{dG}{da_1} = g + (\Sigma a_i)\frac{dg}{d\gamma_1}\frac{\partial\gamma_1}{\partial a_1};$$

$$\gamma_1 = \frac{a_1}{\Sigma a_i};$$

$$\frac{\partial\gamma_1}{\partial a_1} = \frac{\Sigma a_i - a_1}{(\Sigma a_i)^2} = \frac{1-\gamma_1}{\Sigma a_i};$$

i.e.

$$\bar{g}_1 = g + (1-\gamma_1)\frac{dg}{d\gamma_1}. \qquad (5)$$

In particular when $\frac{dg}{d\gamma_1} = 0$, $\bar{g}_1 = g$.

For extensive properties (volume, heat capacity, internal energy etc.), related to 1 mol of substance, general equations are deduced in chemical thermodynamics relating molar properties and compositions of a solution to the partial molar properties of the components. Equation (5) is essentially the partial form of this general equation.[1] However, as may be seen from the exposition above, it is applicable not only to properties connected with the quantity of substance but also to purely intensive properties as, for example, the refractive index, dispersion, hardness etc, though under known reservations, in the form of Equation 1.

For practical utilization, Equation (5) may be put in the form:

$$\bar{g}_1 = g + (1 - \gamma_1)\frac{\Delta g}{\Delta \gamma_1} . \qquad (5a)$$

In equation 5a the values of g and Δg are determined experimentally, γ_1 is given by the initial composition and $\Delta\gamma_1$ is calculated from the change of composition.

The partial quantities $\bar{g}_1$, calculated from equation 5a have a definite thermodynamic meaning: they represent the change which the properties of the system suffers on addition of the component investigated. In particular cases this quantity may correspond to the particular partial property of the component in the system or in our case to the partial property of the oxide in the glass. It can be assumed that the change in the property of the glass g by the quantity Δg on addition of one of the components is caused by two effects:

1) Difference between the properties of the initial glass and the partial properties of the component introduced into it;

2) Change of the structure of the glass, in the broad sense of this word, as a result of the introduction of the component which causes a change of the properties of the stable components in the initial glass.

The quantity $\bar{g}_1$ corresponds to a true partial property of the component in the glass only in those cases where the second cause is not effective, i.e. where the properties of the initial glass are a linear function of the composition. As a rule this condition is not fulfilled, in particular in the presence in the glass of the oxides TiO_2, B_2O_3, and some others.[2] In the absence of the indicated oxides the role of the second factor is not great in the limited field of composition examined by us, and it may be neglected. Then the quantities $\bar{g}_1$ come near to the real partial properties of the components. The quantities $\bar{g}_1$ for one component change so little with composition that they can be averaged and expressed by definite constant figures; for others, as mentioned above the quantities change according to a definite law. It is useful to distinguish components with comparatively stable and components with quite variable partial properties.

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1) See e.g.: B.F.Dolzh, Chemical Thermodynamics. 134-157 (1950).

2) The peculiar behavior of these oxides in glass will be shown in subsequent papers.

It can be taken as a basis that the quantities $\bar{g}_i$ in cases where they are close to the real partial properties of the components, are essentially characteristic of the chemical nature and the structural state of the components, in our case the oxides, in the glass.

It should be noted again that the concept of " oxides" in the glass, according to our definition, is quite arbitrary. None the less the use of this conception is completely justified and even more so it necessarily follows from the whole exposition. According to the method described above, partial properties of the components, i.e., of the oxides, may be determined, but it is impossible to determine partial properties of the ions or of the coordinate polyhedra formed from them because these are not components. However, the numerical characteristic properties of oxides in the glass cannot reflect the properties of the cations in the corresponding "oxygen environment."

As has been shown above, obtaining true partial quantities $\bar{g}_i$ according to Equation (5a) is conditioned by definite requirements above the quantitative and qualitative change in composition of the glass. In the literature there is very little experimental data satisfying these requirements. Hence the method described can find extremely limited use. However, for determining the partial properties of oxides, other, indirect, methods may be used. Without considerable departure from the truth it may be taken that a number of properties of complex glasses can be arrived at additively from the partial properties of their components (oxides), so long as the oxides TiO_2, B_2O_3, PbO and CdO etc., are absent. Thus if the properties of di-, tri-, and multicomponent glasses are known on the one hand, and the partial property of one of these oxides, calculated from Equation (5a), on the other hand, then by simple calculation from the differences in going from the simple to the more complex systems, the values $\bar{g}_i$ of the other oxides may be found from Equation (4). This method was taken as a basic one for our investigations.

In glass without the presence of the referred-to oxides, whose partial properties vary considerably, the $\bar{g}_i$ values calculated from Equation (5a) in general are in satisfactory agreement with the g_i values found by difference from Equation (4). Thus, here we get a unique solution of the problem. The examination of more complicated cases which do not conform to the limitations in composition mentioned will be made later on.

State and properties of silica in glass. Through the oxides entering into the composition of complex silicate glasses, more complete and certain information concerning the properties of silica can be obtained. The partial properties of silica can be calculated in particular from the results of investigating the properties of binary glass systems. We prepared and investigated such a special series of tri-component glasses from the system Na_2O-BaO-SiO_2, in which the quantity of SiO_2, was systematically varied while the ratio $Na_2O/BaO = 1$ remained constant.

The optical constants of the glasses were measured on a Pulfrich refractometer. The density of the glass was determined by hydrostatic displacement. To determine the average coefficient of expansion between 20 and 4000 we measured the change in length of the sample, in the form of a rod 18 cm long, (improved dilatometer of type GIKI). Pure reagents were used for compounding the charges. The silica was introduced as selected natural quartz or rock crystal. An electric furnace was used for heating the glass, the charge being placed in a platinum crucible and the melt being agitated vigorously.[1]

[1]) In the experimental and technical parts of the work (fusing the glasses and determination of their properties), the results of which will be examined in the present and succeeding papers, the following persons participated: K.A.Shishov, S.S.Kayalova, V.I.Medvedev and O.I.Yakovleva.

The results of determiningthe properties of the glasses which we prepared are set forth in Table 2. From these data the values of the partial quantities g_{SiO_2}, were calculated by means of Equation (5a). For this purpose we used extensively the experimental data of other investigators [7, 8] on the optical properties and density of glass systems; Na_2O-SiO_2 K_2O-SiO_2, Na_2O--CaO-SiO_2.

TABLE 2

Experimental Data on the Properties of some Glasses (our Measurements), Used for Calculating the Partial Properties of Silica

Glass No.	Composition of glass in mol fractions					Properties of glass			
	SiO_2	Li_2O	Na_2O	K_2O	BaO	n_D	d	$(n_F-n_C)\cdot10^5$	$\alpha_{20-100°}\cdot10^7$
1	0.640	0.360				1.5418	2.348	910	122.3
2	0.740	0.260				1.5164	2.315	835	89.7
3	0.800	0.200				1.5015	2.285	793	70.7
4	0.840	0.160				1.4913	2.263	765	-
5	0.612		0.388						182.0
6	0.640		0.360						171.2
7	0.714		0.286						144.0
8	0.778		0.222						115.8
9	0.800		0.200						104.8
10	0.840		0.160						82.0
11	0.740			0.260					155.3
12	0.800			0.200					120.5
13	0.840			0.160					97.0
14	0.640	0.200	0.160			1.5265	2.438	915	-
15	0.600		0.200		0.200	1.5754	3.254	1077	141.0
16	0.652		0.174		0.174	1.5654	3.144	1024	129.4
17	0.700		0.150		0.150	1.5513	3.006	977	114.6
18	0.750		0.125		0.125	1.5357	2.869	-	101.1
19	0.800		0.100		0.100	1.5207	2.726	874	83.8
20	0.840		0.080		0.080	1.5063	2.607	-	67.0

Note: The composition of the glasses here and later is, in the majority of cases, taken from the quantities weighed out. Practice showed that with due caution in the fusing of the glass the deviation between the analytical and synthetic data was not considerable and lay within the limits of analytical error.

The results of calculation of partial properties of silica are shown by the position of the points in Fig. 1.

For the partial properties of silica we introduced the following designation; $\bar{N}_{SiO_2}$ (partial refractive index), $\bar{V}_{SiO_2}$ (partial molar volume), D_{SiO_2} (partial mean dispersion), α_{SiO_2} (partial mean coefficient of expansion between 20 and 400°)

Before we proceed to an examination of the results it must be emphasized that the partial properties of the components cannot be determined accurately. For example, the deviation of 0.3% of the true densities of Glasses 15 and 16 from the measured one causes an error of 2.3% in the determination of $\bar{V}_{SiO_2}$ in this interval of composition; the actual difference of coefficient of

expansion of these same glasses differs from that measured by $1.5 \cdot 10^{-7}$ (this is 1% of the value of α for the glass), so that the error in the determination of α_{SiO_2} will be $10 \cdot 10^{-7}$, etc. Errors in the determination of the composition of the glass are also reflected just as strongly in the relevent partial quantities.

In spite of these unfavorable circumstances, Fig. 1 give a clear picture of the partial properties of silica. The partial values $\bar{N}_{SiO_2}$ change little but always in the direction of a decrease as the SiO_2 content in the glass increases.

A small change, but in the opposite direction, is shown by the value of $\bar{V}_{SiO_2}$.

The calculated values of $\bar{\alpha}_{SiO_2}$ show large fluctuations in going from one glass to another, and they are determined with small accuracy. All the same a considerable diminution of the value of α_{SiO_2} with increase in the mol fraction of SiO_2 in the glass was observed.

In contrast to the properties mentioned, the quantities $\bar{D}_{SiO_2}$ vary around a constant value, practically equal to the dispersion of the pure glassy silica. In general, for the majority of the properties of glass, the partial properties of silica appear to be variable.

This conclusion has considerable importance because it demonstrates the inaccuracy of the previous assumptions about the invariance of the properties of silica in glass, which have been made by the majority of investigators.

The changes of the properties of silica in glasses of different composition, strictly speaking, are not identical. However, relative to the task of elucidating a more general dependence connecting the properties of glass with their composition, and bearing in mind the practical aim of calculating properties from composition, we consider it necessary to deal with simplified observations and averaged quantitative characteristic properties.

Simplification and averaging appear to be inevitable measures to which it is necessary to resort for the examination of the properties of such complicated systems as glasses, where there are such innumerable possible combinations in composition.

The essence of the simplifications and averaging which we have used is based on the following two assumptions:

1) With diminution of the quantity of silica in the glass from 100 to 67 mol % ($f_{Si} = 0.5—0.4$) the partial quantities $\bar{N}_{SiO_2}$, $\bar{V}_{SiO_2}$, $\bar{\alpha}_{SiO_2}$, change linearly, along one and the same straight line in all silicate glasses (at the initial points, i.e. at 100% SiO_2, these values obviously correspond to the properties of pure quartz glass).

2) Over the composition interval poorer in silica (from 67 to about 45 mol % SiO_2) the averaged partial properties of silica remain constant and identical for all silicate glasses. The value of the partial properties of silica in this composition interval are determined as arithmetical means from the calculated experimental data for the corresponding glasses; they are $\bar{N}_{SiO_2} = 1.475$,[1] $\bar{V}_{SiO_2} = 26.1$ CM^3/MOl, $\bar{\alpha}_{SiO_2} = 38 \cdot 10^{-7}$.

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[1]) It is important to note that these $\bar{N}_{SiO_2}$ values agree with those found earlier by Denkin [6] by graphical analysis of extensive statistical material concerning the effect of small additions of oxides on the optical constants of optical glasses.

The limits within which the averaged values of the partial properties of silica $\bar{g}_{SiO_2}$ in silicate glasses change are set forth in Table 3.

TABLE 3

Approximate figures for characteristic partial properties of silica in silicate glasses

Average values of g_{SiO_2}			
$\bar{N}_{SiO_2}$	$\bar{V}_{SiO_2}$	$\bar{D}_{SiO_2} \cdot 10^5$	$\bar{\alpha}_{SiO_2} \cdot 10^7$
1.4585-1.475	27.25-26.10	675	5-38

Note: The values of $\bar{D}_{SiO_2}$ are taken as unchanged at all compositions, and equal to the dispersion of pure glassy silica.

The variation of the quantities $\bar{N}_{SiO_2}$, $\bar{V}_{SiO_2}$, $\bar{D}_{SiO_2}$, $\bar{\alpha}_{SiO_2}$ in their simplified and averaged form and in accordance with the assumptions we have made are shown graphically by the solid line in Figure 1.

These changes can be expressed by the following simple equations:

$$\bar{N}_{SiO_2} = 1.475 - 0.0005\ (a - 67); \quad (6)$$

$$\bar{V}_{SiO_2} = 26.1 + 0.035\ (a - 67); \quad (7)$$

$$\bar{\alpha}_{SiO_2} \cdot 10^7 = 38 - 1.0\ (a - 67), \quad (8)$$

where $a > 67$ and expresses the molar percent SiO_2 content in the glass.

As follows from the distribution of the points on the figures, the actual course of the changes of the average partial properties of silica (dotted lines) differ somewhat from the simplified course assumed by us. However, these deviations only slightly exceed the possible error of experiment and the advantages obtained by simplification in the calculations are very substantial.

The experimental material given above can be given a definite theoretical interpretation. According to contemporary ideas there are no discreet molecules of SiO_2 in silicate glasses. The basic structural unit of a silicate glass is the SiO_4 tetrahedron. Pure quartz glass is entirely composed of such tetrahedra in which each of the oxygen summits is common to two neighboring tetrahedra. Figure 2a is a diagrammatic representation of the surface of the SiO_4 tetrahedra in quartz glass. Inside the sphere is shown a 'molecule' of SiO_2. Each 'molecule' consists of one silicon ion Si^{4+} and four oxygen half ions equidistant from the Si^{4+}. These oxygen ions are said to be 'double-bonded'. On introduction of the first portion of the oxides Me_2O or MeO into quartz glass one summit in a SiO_4 tetrahedra is weakened, because some of the oxygen ions, said to be single-bonded, find themselves in the neighborhood of metal ions Me^{2+} Me^{1+}, the electric field strength around which is weaker than that around Si^{4+} (figure 2,b). The quantity of these tetrahedra increases as the quantity of oxides Me_2O + MeO in the glass increases. The glass skeleton having composition $1(Me_2O + MeO) \cdot 2SiO_2$ i.e. containing around 67% SiO_2 on the average is constructed of tetrahedra with one 'weakened' summit. This process of change is characteristic of silicon-oxygen glasses and is reflected in the properties of SiO_2 in the glass. In the structural element Si-O-Me the Si-O distance should be less than in the elements Si-O-Si[1]. It is known that introduction of the oxides Me_2O and MeO into quartz glass should lead to slight

[1]) See next page for footnote.

distortion of the SiO_4 tetrahedra, causing them to be compressed. Hence $\bar{V}_{SiO_2}$ slightly diminishes and $\bar{N}_{SiO_2}$ somewhat increases. The ability of SiO_4 tetrahedra to move about a mean position under the influence of temperature should increase considerably as a result of the weakening of one of the summits. This is also demonstrated by the value of $\bar{\alpha}_{SiO_2}$. The partial coefficient of expansion of SiO_2 in a complex glass is a few times larger than the coefficient of expansion of free glassy silica.

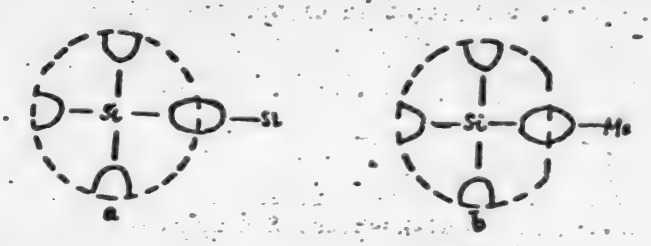

Fig.2. Schematic representation of the possible effect of compression of a SiO_4 tetrahedra in a glass.
a) Quartz glass; b) quartz glass after introduction into it of the oxide Me_2O or MeO.

With further increase of the amount of the oxides Me_2O and MeO in the glass above 33%, the second summit of the tetrahedra weakens, then the third, and finally the fourth. However, such structural changes are little reflected in the $\bar{g}_{SiO_2}$ values. More strictly speaking this effect can be established only with difficulty because the errors introduced into the calculation by the other oxides begin to play a predominant role.

The $\bar{g}_{SiO_2}$ values in this case may be taken as constant.

Taking the law for change of $\bar{g}_{SiO_2}$ as identical for all silicate glasses, we have arrived at the same conclusions that the properties of the SiO_4 tetrahedra do not depend on the nature of the cations Me^{1+} and Me^{2+} contiguous with the single-bonded oxygen ions. This assumption is near to the truth relative to such properties as the refractive index and molar volume inasfar as the total change of $\bar{N}_{SiO_2}$ and $\bar{V}_{SiO_2}$ is small (respectively 1.1 and 4.4%). In relation to these properties our assumptions can possibly be extended even to the cations Al^{3+}, B^{3+}, Ti^{4+} etc. This cannot be said about the relative coefficient of expansion[2]. However it is still not possible to express in

[1]) In the X-ray investigations of the structure of glass, apparently, it is impossible to obtain direct data showing differences in the distances mentioned. X-ray analysis of glass gives information only about the average state but has nothing to say about accurate details of structure. Differences between average separations of Si-O in SiO_4 tetrahedra (Figure 2 a and b) lie within the accuracy of experiment which is insufficient to decide the question. Experiment gives the average Si-O distance in glasses as 1.62 A $\pm$ 0.02A. Such experimental uncertainty just about covers the possible effect of a 4% compression of SiO_4 tetrahedra.

However, in general crystal chemistry, the shortening effect on the interionic distance examined by us, although manifested only under definite conditions, has still not been sufficiently studied. This phenomenon, according to Goldschmidt, is an example of 'controlarization' or 'second polarization'.

[2]) In reality strict examination of the position of the points in Figure 1 shows that even in relation to $\bar{V}_{SiO_2}$ and $\bar{N}_{SiO_2}$ the effect of different cations is different. There is a greater diminution of $\bar{V}_{SiO_2}$ in potassium glasses and a smaller one in lithium glasses (an inverse relationship was observed for $\bar{N}_{SiO_2}$). These facts are in complete concordance with our scheme, explaining the observation by the compression of the SiO_4 tetrahedra.

quantitative form the effect of the nature of the cation on the properties of SiO_2 in glass. For this reason the possibility of theoretical prediction of the value of the coefficients $\bar{\alpha}_{SiO_2}$ calculated from Equation (8) is lowered. Their practical value is completely maintained.

This picture of the change of structure of the silicon-oxygen skeleton and of the SiO_4 tetrahedra themselves on introduction of oxides of the uni- and divalent elements, as described by us, expresses an idealized averaged state of the systems, taken as a whole. For example, instead of the initial formation of tetrahedra with one weakened summit (this corresponds to bi-silicates) tetrahedra with two weakened summits may be formed immediately (this corresponding to metal-silicates), but the quantity of these would be twice as small. However, these complications of the basic process can be neglected in making generalized correlations.

Some part of the silica and other components of glasses, as shown by different investigators (Akad. A.A. Lebedev, E.A. Porai-Koshits, N.A.Shishakov and others) may be found in the form of crystallites. The above exposition of the state of SiO_4 tetrahedra does not contradict this.

Thus, the graphical material presented above and Equations (6-8) proposed by us, approximately characterize the partial properties of silica, and they have not only a known experimental significance but are also in agreement with definite theoretical ideas.

However, the most important results of our investigation involving the introduction of other oxides into, and the study of their properties in, glass, are the conclusions about the properties of silica formulated above.

SUMMARY

1) It has been shown that the concept of partial quantities, reflecting the partial properties of components in solution, can be used with certain reservations not only in relation to extensive, but also to intensive properties of solutions (glasses).

2) With the help of certain simplified observations, and averaging of the numerical results of the characteristic properties, simple approximate equations are obtained defining the partial properties of SiO_2 as a function of the molar content of SiO_2 in the glasses.

3) An attempt at a theoretical interpretation of the correlations found has been made, according to which the partial properties of SiO_2 depend not only on the concentration of SiO_2 in the glasses but also on the nature of other components present. However, taking into account the fact that in relation to the properties examined by us (excluding the average coefficient of linear expansion α) the role of the second factor is small for the practical aim we have in mind (calculation of properties of glasses from their composition), it can be concluded that the proposed equations are approximately correct for all silicate glasses.

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PREPARATION OF SODIUM MANGANATE AND PERMANGANATE BY ANODIC SOLUTION OF METALLIC MANGANESE

B. I. Agladze and G. M. Domanskaya

In a previous communication [1] we presented the result of experiments on the anodic solution of metallic manganese in caustic potash. The present communication is devoted to experiments on the electrolysis of aqueous solutions of NaOH and Na_2CO_3 with manganese anodes.

The known method of preparing sodium permanganate consists in fusing NaOH with pyrolusite in the air [2]. As in the case of potassium manganate, in this method also the whole quantity of MnO_2 contained in the pyrolusite is not oxidized to sodium manganate [3]. Good results have been shown by an electrochemical method for preparing sodium permanganate based on the oxidation of solutions of manganate [4]. Other methods of preparing sodium permanganate and manganate are met with in the literature [5].

EXPERIMENTAL

The set-up which we usedfor carrying out our experiments, as well as the method of analysis of the products of electrolysis, were described by us in the paper in which the results of experiments with potassium solutions were presented [1]. Plates of electrolytic metallic manganese containing 99.9% Mn were used as anodes; the NaOH and the Na_2CO_3 were technically pure materials. Sodium manganate was obtained in strong alkali solutions of caustic soda; sodium permanganate was formed in weak NaOH and in Na_2CO_3 solutions.

Effect of concentration of electrolyte. In table 1 are set forth the results of experiments made to elucidate the effect of caustic soda concentration on the anodic solution of manganese. Examining the data obtained we see that, at an anode current density of 4 A/dm^2, a change of the concentration of alkali from 1.7 to 36% causes almost a tenfold increase in the oxidizing power of the solution. This sharp change of the oxidizing power was observed in spite of the fact that the oxidizing power of the permanganate ion [by reduction to Mn(II)] relative to the oxidizing power of the manganate ion is in the ratio of 5/4 and consequently, the oxidizing power of a manganate solution obtained in concentrated alkali should be lower than in weak alkali solutions containing the same quantity of Mn but as Mn (VII). Consequently, while the oxidizing power of the solutions obtained in Experiments 17 and 11 are in the ratio of 1/10, the quantities of manganese (anode dissolving in 2.2% alkali with formation of MnO_4^- and in 36% with formation of MnO_4^{2-}) are in the ratio of 1/12.5.

Plotting the data of these experiments as a graph of concentration of electrolyte against its oxidizing power, we obtain a series of curves (Figure 1) which indicate a continuous growth of the oxidizing power of the solution with increase in concentration of alkali. It should be noted that comparison of the data obtained with solutions of KOH and NaOH showed that the process of oxidation in caustic soda is smoother than in caustic potash. Thus, in experiments with KOH as an electrolyte, after passage of 1 Ah the oxidizing

power of the solution obtained was less than the oxidizing power of the solution after a similar experiment with NaOH as an electrolyte, but through which 0.645 Ah was passed.

TABLE 1

Effect of concentration of electrolyte on the process of anodic solution of manganese in solutions of NaOH

Series No.	Expt. No	Concentration of electrolyte (in %)	Duration of expt. (in mins)	Current passed (in Ah)	Current density (in A/dm²) Anode	Current density (in A/dm²) Cathode	Oxidizing power of the product obtained (in ml of 0.1 $Na_2C_2O_4$)
I	1	24	30	0.2	5.7	40	18.0
	2	18		0.2	5.7	40	10.4
	3	12		0.2	5.7	40	8.4
II	4	50	90	1.33	12.2	39	178.2
	5	36			4.1		52.8
	6	24					33.0
	7	12					16.2
	8	9					12.6
	9	7					13.2
	10	6					12.0
III	11	36		0.645	4.0	14	45.6
	12	18					17.1
	13	12					12.6
	14	9					9.0
	15	7					9.3
	16	4					6.3
	17	2.2					4.5
	18	1.7					4.8

The results of experiments carried out with solutions of K_2CO_3 are set forth in Table 2. In Figure 2 the results of seven of the experiments reported in the Table are presented graphically. Examination of the data of this series shows analogies with the data obtained with solutions of K_2CO_3. Here, using an electrolyte of moderate concentration, the current efficiency was maintained at 24-28%. It should be mentioned that when we used saturated solutions of alkali carbonate, crystallization of permanganate occurred. The crystals collected on the floor of the cell and covered part of the anode.

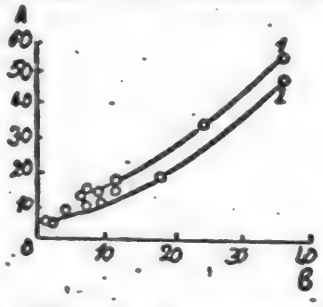

Fig.1. Effect of concentration of NaOH on the oxidizing power of the product obtained.
A) Oxidizing power (in ml of 0.1 solution of $Na_2C_2O_4$); B) concentration of NaOH(in %). 1) Experiments of series II; 2) Series III.

Effect of temperature. The experiments for the elucidation of the effect of temperature were carried out with 45.5% NaOH at an anode c.d. of 7.1 A/dm². In all experiments of this series solutions of sodium

manganate were obtained as a result of electrolysis When the temperature rose from 10 to 95° the current efficiency for sodium manganate increased from 32.8 to 58.2% and the potential across the bath decreased from 5.2 V at 10° to 2.2 V at 95°. However, raising the temperature above 65° cannot be recommended because the rate of reduction of Mn (VI) at the cathode is increased by a rise in temperature and the chemical decomposition of manganate by the slime and the impurities contained in the alkali is also accelerated. With elevation of temperature the quantity of slime also increases. The appearance of a larger quantity of slime and a sharp lowering of the product yield (from 89% at 65° to 65% at 95°) makes the expediency of using a higher temperature doubtful, in spite of the improved current efficiency and the increase in the quantity of manganese going into solution, as well as of the quantity of manganate formed.

TABLE 2

Effect of concentration of electrolyte on the process of anodic solution of manganese in Na_2CO_3 solutions

Expt. No.	Concentration of Electrolyte (in %)	Voltage (V)	Current passed (in amp-hr)	Quantity of Mn (in g) leaving the anode and going: into solution as $NaMnO_4$	Quantity of Mn (in g) leaving the anode and going: into the slime	Current efficiency for $NaMnO_4$ (in %)	Product yield (in %)	Consumption of energy (in kWh/kg$NaMnO_4$)
1	26.0	—	0.75	0.031	0.007	14.1	80	—
2	21.5	5.0	0.8	0.059	—	25.3	—	26
3	19.7	4.9		0.056	—	23.9	—	27
4	14.6	4.8		0.066	0.008	28.4	90	23
5	12.5	4.3		0.060	0.012	25.8	84	21
6	10.0	4.7		0.062	0.011	26.6	85	23
7	3.5	7.2		0.032	0.015	13.6	68	70

The results of the experiments of this series are set forth in Table 3. From them curves have also been constructed and are presented in Figure 3.

In the preparation of sodium permanganate by the anodic solution of electrolytic manganese in solutions of Na_2CO_3, the effect of temperature was confirmed by us in two series of experiments, the results of which are set forth in Table 4. The first series was made with an anode c.d. of 14 A/dm^2, and

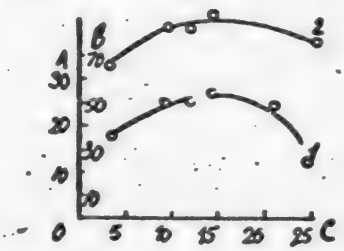

Fig.2. Effect of concentration of electrolyte on the process of anodic solution of manganese in solutions of Na_2CO_3.
A) Current efficiency (in %); B) product yield (in %); C) concentration of Na_2CO_3 in %. 1) Current efficiency for $NaMnO_4$ (in %; 2) product yield (in %)

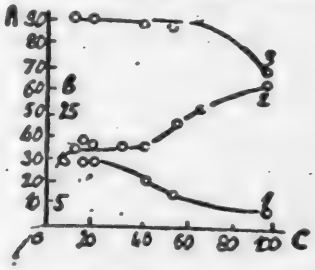

Fig.3. Effect of temperature on the process of anodic solutions of manganese in NaOH.
A) Current efficiency (in %); B) energy consumption (in kW-hr/kg Na_2MnO_4); C) temperature (in °). 1) Consumption of energy (in kw-hr/kg Na_2MnO_4); 2) current efficiency for Na_2MnO_4 (in %); 3) product yield (%).

TABLE 3.

Effect of temperature of electrolyte on the process of anodic solution of manganese in 45.5% NaOH

Current density at the anode 7.1 A/dm², at the cathode 31 A/dm²

Expt. No.	Temperature (in °)	Voltage (V)	Duration of expt. (in mins)	Quantity of Mn (in g) leaving the anode and going: into solution as Na_2MnO_4	Quantity of Mn (in g) leaving the anode and going: into the slime	Current efficiency for Na_2MnO_4	Product yield (in %)	Consumption of energy kw-hr/kg Na_2MnO_4
1	10-12	5.2	60	0.109	0.011	32.8	90.9	—
2	14	5.0	72	—	—	36.5	—	13.5
3	18	5.0	60	0.123	0.0137	33.9	90	13.5
4	32-35	4.5	60	—	—	35.8	—	11.0
5	41	3.5	60	0.116	0.017	34.2	87	10.0
6	53-55	3.0	60	0.150	0.022	44.0	87	6.6
	64-66	2.9	60	0.168	0.021	49.6	89	5.7
	95-96	2.2	60	0.197	0.105	58.2	65	3.8

TABLE 4

Effect of temperature of electrolyte on the anodic solution of manganese in 13% Na_2CO_3

Duration of experiments: 60 minutes.

Expt. No.	Temperature of expt. (in °)	Voltage	Current density (in A/dm²): Anode	Current density (in A/dm²): Cathode	Quantity of Mn (in g) leaving the anode and going: into solution as $NaMnO_4$	Quantity of Mn (in g) leaving the anode and going: into the slime	Current efficiency for $NaMnO_4$ (in %)	Product yield (in %)
1	21-23	—	14	85	0.093	0.015	22.5	86
2	52-55	6.4	14	85	0.107	—	26.0	—
3	62-64	6.3	14	85	0.113	0.019	27.5	86
4	71-74	5.4	14	85	0.082	0.017	19.9	83
5	82-84	5.3	14	85	0.075	0.013	18.3	85
6	90-85	—	14	85	0.079	0.038	19.2	67
7	18	—	4.2	21	0.025	0.004	28.5	87
8	23	—	5.0	25	0.044	0.0036	28.5	92
9	35-39	—	4.2	21	0.036	0.006	24.0	86
10	42	—	5.0	25	0.044	0.005	25.1	90
11	59	—	5.0	25	0.036	0.010	20.8	78
12	66-68	—	4.6	23	0.035	0.008	21.6	81
13	75	—	4.2	21	0.034	0.009	17.2	79
14	74-78	—	4.2	21	0.025	0.011	17.0	70

the second at 4.2-5 A/dm². In both cases 13% Na_2CO_3 solution was used as an electrolyte. When working at temperatures within the limits 18-40° a current efficiency of 28.5 to 24% was obtained. Further elevation of the temperature lowered this efficiency (17% at 78°).

When the temperature is raised the product yield falls from 87% at 18° to

70% at 78°. Similarly, the total quantity of anodically dissolved manganes falls and the quantity of slime increases. The increase of the quantity of slime formed at higher temperatures occurs not only at the expense of the electrochemical production of Mn^{3+} and Mn^{4+} ions, but also as a result of the chemical decomposition of permanganate by heat in alkali solution.

Thus, 15-40° should be taken as the optimum temperatures for the preparation of sodium permanganate.

Effect of current density. The data of Table 5 show the effects of change of anode c.d. on the process of electrolysis in 40% NaOH. We varied the c.d. from 0.65 to 21.0 A/dm^2. It should be mentioned that at the relatively small c.d. of 0.65 A/dm^2 the formation of sodium manganate is rather intense, in contrast with the rate of formation of potassium permanganate (current efficiency 27.5%). At 2 A/dm^2 and with a potential of 2.8V across the cell the current efficiency increased to 35.8%. At this c.d. a smaller consumption of energy was observed - 5 kw-hr/kg of sodium manganate. Further increase of the c.d. had no significant influence on the current efficiency (maximum value of 39.3% was observed at an anode c.d. of 5.27 A/dm^2), but increased the energy consumption, approaching 16 kw-hr/ kg manganate at a c.d. of 21 A/dm^2.

TABLE 5

Effect of anode c.d. on the anodic solution of manganese in 40% NaOH. Duration of experiments: 95 minutes.

Expt. No.	Temperature (in °)	Voltage (in V)	Current density (in A/dm^2)		Yield of Na_2MnO_4 (in g)	Current efficiency for Na_2MnO_4 (in %)	Energy consumption (in kw-hr kg Na_2MnO_4)
			Anode	Cathode			
1	2.2	16	0.65	1.66	0.027	27.5	7.8
2	2.4		1.06	2.7	0.040	25.0	9.6
3	2.8		2.04	4.9	0.104	35.8	5.0
4	3.3		2.6	6.7	0.159	38.2	8.2
5	3.8	18	5.27	13.5	0.322	39.3	9.5
6	4.4	16	7.7	20.3	0.480	38.8	11.0
7	4.7	18	10.5	27.5	0.623	38.8	12.0
8	5.2	20	13.2	33.8	0.756	37.1	13.9
9	5.3	22	15.8	40.6	0.879	35.9	14.5
10	5.9	25	21.0	52.8	1.156	36.2	16.0

On the basis of this series of experiments, we recommend an anode c.d. of 2-5 A/dm^2 for the preparation of sodium manganate by anodic solution of manganese in NaOH.

The effect of change of anode c.d. on the process of anodic formation of sodium permanganate was also studied in experiments carried out with 15% Na_2CO_3, at anode c.d's of 2.9-25 A/dm^2 (Table 6 and Fig. 4). By raising the c.d., the current efficiency was raised from 21.8% at 2.9 A/dm^2 to 31.5% at 17 A/dm^2. However, the potential across the cell increased from 3.5 to 7.4 V and the specific energy consumptions increased correspondingly. In experiments carried out at 25° the product yield was 90-95%.

Effect of the ratio of surfaces of anode and cathode. Table 7 contains results of experiments carried out with different values of the ratio of anode to cathode current density. These experiments on the production of sodium manganate were made with 47% NaOH. The anode c.d. was kept constant at 9 A/dm^2,

TABLE 6

Effect of anode c.d. on the anodic solution of manganese in 15% Na_2CO_3. Duration of experiments: 60 minutes

Expt. No.	Temperature (in °)	Voltage (in V)	C.D. (in A/dm²)		Quantity of Mn (in g) leaving the anode and going:		Current efficiency for $NaMnO_4$ (in %)	Product yield (in %)	Consumption of energy in Kw-hr/kg $NaMnO_4$.
			Anode	Cathode	Into solution as $NaMnO_4$	Into the slime			
1	24	3.5	2.9	6.6	0.0128	0.0016	21.8	88	21.2
2	25	4.8	5.7	13.3	0.0302	0.0030	25.7	91	24.3
3	24	6.0	8.7	20.7	0.0470	0.0033	25.8	96	30.8
4	26	6.2	11.4	26.5	0.0620	0.0040	24.3	94	31.0
5	27	7.2	14.4	33.0	0.0920	0.0081	26.0	92	29.0
6	25	7.4	17.0	40.0	0.1110	0.0060	31.5	95	30.6
7	42-46	4.5	8.3	25.0	0.0330	0.0080	22.7	81	26.5
8	43-46	4.7	13.3	40.0	0.5700	0.0047	24.0	90	26.3
9	44-45	—	18.3	55.0	0.0830	0.0130	26.0	87	—
10	43-47	—	25.0	75.0	0.1300	0.0130	29.8	91	—

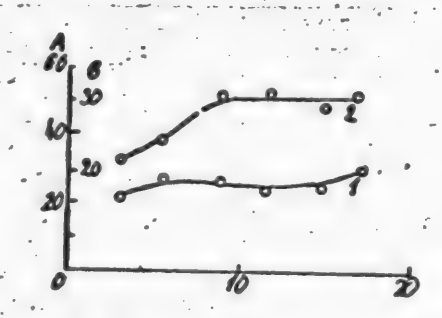

Fig. 4. Effect of anode c.d. on the anodic solution of manganese in Na_2CO_3 solutions.
A) Current efficiency for $NaMnO_4$ (in %); B) Consumption of electrical energy (in kw-hr/kg); C) anode c.d. (in A/dm²). 1) Current efficiency for $NaMnO_4$ (in %); 2) energy consumption in kw-hr/kg $NaMnO_4$).

while the cathode c.d. in each experiment was changed in succession to 90, 26.6, 11.4 and 7.6 A/dm².

Comparison of all such experiments of this series (current and product efficiency, specific energy consumption) leads to the conclusion that the best results are obtained when the area of the anode is three times that of the cathode, i.e. when the ratio of anode to cathode c.d. is 0.3-0.4. When this is so the current efficiency is 40.5%, the specific energy consumption is 12 kw-hr/kg, and the product yield is 93%.

Effect of separation between the electrodes and stirring of the electrolyte. We carried out 4 experiments with 47% NaOH solution at different inter-electrode distances (Table 8). An analysis of the results of these experiments shows that with increase in the separation of the electrodes the current efficiency is only slightly increased; however, this increase did not compensate the increase in energy consumption, due to the increase in the resistance of the electrolyte.

The results of three experiments to find out the effect of stirring the electrolytes and rotating the anodes are presented in Table 9. The data of this table indicates that, in the case of an electrolyte containing NaOH, the effect of mixing the electrolyte is very weak. The current efficiency increases altogether by 1% and the product yield by 2.5%.

TABLE 7

Effect of the ratio of anode to cathode c.d. on the anodic solution of manganese in 47% NaOH

Duration of experiment: 1 hour. Temperature: 16°

Expt. No.	Ratio of anode to cathode c.d.	Current density (in A/dm^2)		Quantity of Mn (in g) leaving the anode and going:		Current efficiency for Na_2MnO_4 (in %)	Product yield (in %)	Consumption of energy (in kw-hr/kg Na_2MnO_4)
		Anode	Cathode	into solution as Na_2MnO_4	into the slime			
1	0.10	9	90.0	0.103	0.0090	38.2	92.0	15.0
2	0.34	9	26.6	0.109	0.0081	40.5	93.0	12.0
3	0.79	9	11.4	1.090	0.0127	33.6	88.0	12.6
4	1.18	9	7.6	0.096	0.0097	35.6	90.6	10.5

TABLE 8

Effect of separation between the electrodes on the anodic solution of metallic manganese in 47% NaOH

Temperature: 24-27°. Anode c.d. 5.7 A/dm^2, cathode c.d. 28 A/dm^2

Expt. No.	Distance between electrodes (in cm)	Duration of experiment (in minutes)	Voltage (in V)	Quantity of Mn (in g) leaving the anode and going:		Current efficiency for Na_2MnO_4 (in %)	Product yield (in %)	Consumption of energy (in kw-hr/kg Na_2MnO_4)
				into solution as Na_2MnO_4	into the slime			
1	5.2	90	5.8	0.142	0.0084	35.0	94.7	14.7
2	3.5	90	5.2	0.138	0.0089	34.2	94.0	16.0
3	2.2	90	4.9	0.129	0.0060	32.0	95.5	15.0
4	0.8	120	4.4	0.171	—	31.7	—	13.6

Effect of duration of experiment. In Table 10 are the results of 7 experiments carried out with concentrated (50%) NaOH at an anode c.d. of 12.2 A/dm^2. The quantity of electrolyte in each experiment of this series was 30 ml. The current efficiency for experiments lasting 20 minutes was 54.2%, dropping to 44.6% when the experiment was carried on for two hours. It should be noted that these experiments were carried out under conditions in which the electrolytes heated up; hence the experiments were carried out at 46-55°. It is possible that at this temperature there was a partial decomposition and cathodic reduction of the manganate formed.

Table 11 contains results of an analogous series of experiments, carried out at constant temperature (30°) with 46% NaOH and with an increased quantity of electrolyte (100 ml). It is evident from this table that although some decrease of the current efficiency was observed between the first and second hour, the magnitude of the current efficiency in the succeeding 7 hours scarcely changed, relative to a small decrease in the product yield.

TABLE 9

Effect of stirring the electrolyte and rotating the anode on the process of anodic solution of manganese in 47% NaOH

Expt. No.	Temperature (in °)	Duration of experiment (in minutes)	Current density (in A/dm²)		Quantity of Mn (in g) leaving the anode and going:		Current efficiency for Na_2MnO_4 (in %)	Product yield (in %)	Remarks
			Anode	Cathode	into solution as Na_2MnO_4	into the slime			
1	20	90	8.7	25	0.159	0.013	38.0	92.5	Electrolyte not stirred
2	18	90	9.4	25	0.155	—	38.2	—	Electrolyte stirred with a stirrer rotating at 120 rpm.
3	18	90	8.7	25	0.158	0.008	39.1	95	Anode rotating.

TABLE 10

Effect of duration of experiment on the anodic solution of manganese in 50% NaOH

Temperature of experiment: 46-55°. Potential 3.8 V. Anode c.d. 12.2 A/dm². Cathode c.d. 45 A/dm²

Expt. No.	Duration of Experiment (in minutes)	Na_2MnO_4 obtained (in g)	Current efficiency for Na_2MnO_4 (in %)
1	20	0.179	54.2
2	20	0.176	53.3
3	20	0.183	55.6
4	40	0.351	52.4
5	60	0.505	49.6
6	100	0.925	46.5
7	120	—	44.6

The long-period experiments were performed with 46% NaOH at an anode c.d. of 6 A/dm². The electrolysis was carried on for 46 hours; during this time 27.6 amp-hr was passed through the solution. Part of the electrolyte was withdrawn at intervals and fresh caustic soda added. The general quantity of electrolyte used in this experiment was 500 ml. The current efficiency was 30.3%, the product yield 80%. No increase of the potential across the cell was observed up to the end of the electrolysis: it was 3.6 V at the beginning and 3.4 V at the end. The product of electrolysis was sodium manganate. At the end of the experiment both anode and cathode were covered with a thin layer of manganese dioxide. The surface of the immersed part of the anode at the end of the experiment had changed from 10 to 8.5 cm² as a result of solution, an effect which somewhat raised the c.d.

Electrolysis with anodes of cast electrolytic manganese. In all the above experiments, electrolytic manganese plates were used as anodes. The direct use of cathodic electrolytic manganese would be difficult in industry in view of the brittleness and small thickness of these plates. It is true that it is possible to obtain metallic manganese by electrolysis from an alkaline bath, in which the anode consists of a steel sheet on which manganese is deposited; however, since this has a number of disadvantages, we attemped to prepare anodes derived from electrolytic manganese by re-melting the latter. We prepared manganese castings in the form of four-sided bars. The composition of the metal after melting was (in %):.

Mn	96.91	P	0.021
Fe	0.28	S	0.008
Si	0.13	Ca	0.36

Residue – C, Al, Mg, H_2 and O_2.

TABLE 11

Effect of duration of experiment on the anodic solution of manganese in 46% NaOH Temperature 30°. Anode c.d. 7.5 A/dm². Cathode c.d. 20 A/dm². Voltage 3.4 V

Expt. No.	Duration of experiment (in minutes)	Quantity of Mn (in g) leaving the anode and going: into solution as Na_2MnO_4	Quantity of Mn (in g) leaving the anode and going: into the slime	Current efficiency for Na_2MnO_4 (in %)	Product yield (in %)
1	60	0.072	0.007	42.0	88
2	120	0.116	0.015	34.2	—
3	270	0.275	0.028	36.3	91
4	465	0.444	0.039	35.3	82

TABLE 12

Effect of the electrode material on the anodic solution of manganese in 46% NaOH and 15% Na_2CO_3

Electrode material	Electrolyte	Voltage (in V)	C.d. (in A/dm²) Anode	C.d. (in A/dm²) Cathode	Quantity of Mn (in g) leaving the anode and going: into solution as Na_2MnO_4 or $NaMnO_4$	Quantity of Mn (in g) leaving the anode and going: into the slime	Current efficiency for Na_2MnO_4 or $NaMnO_4$ (in %)	Product yield (in %)
Plates of electrolytic manganese	NaOH	3	8.3	17	0.117	0.012	34.8	91
	Na_2CO_3	4.3	10.0	20	0.085	0.013	27.8	87
Cast electrolytic manganese	NaOH	3	10.0	17	0.110	0.012	32.6	90
	Na_2CO_3	4.3	12.0	20	0.079	0.013	26.0	86

These castings were used as electrodes. The results of experiments carried out with plates of electrolytic manganese as electrodes in parallel with these bars of cast manganese are presented in Table 12. In this series of experiments the value of the anode c.d's. did not coincide, but this could have no notable effect on the result.

Use of cast electrolytic manganese as an anode did not lower the performance of electrolysis, in spite of the somewhat poorer quality of the metal due to the considerable quantity of impurity in it.

In conclusion it should be noted that the slime obtained in the anodic solution of manganese, containing manganese dioxide, may have practical application since it is pure and has a number of valuable properties. In all the experiments described we use anodes prepared from electrolytic manganese plates obtained by our method.

SUMMARY

[1] When using electrolytic metallic manganese as an anode no passivation of the electrode was observed, in contrast to the behavior of ferromanganese and other manganese alloys.

[2] In the anodic solutions of manganese in solutions of Na_2CO_3 and dilute solutions of NaOH, sodium permanganate was formed while in concentrated solutions of NaOH manganate was formed.

[3] In the electrolysis of alkali solutions with manganese anodes, apart from the solution of manganese as compounds in which it has a high oxidation number, a slime is formed mainly of manganese dioxide. With increase of the concentration of NaOH in the electrolyte, the yield of Na_2MnO_4 increases. Best results for the yield of Na_2MnO_4 are obtained when the strength of Na_2CO_3 in the electrolyte is 10-15%.

[4] The optimum temperature for obtaining sodium manganate by electrolysis of NaOH is 50-60°; with increase of temperature from 65 to 95° the current efficiency increased from 49 to 58%, but the yield of slime sharply increased as well. The quantity of the anodic manganese going into the slime increased from 11% at 65°, to 35% at 95°. For obtaining $NaMnO_4$ by electrolysis the optimum temperature seems to be 15 to 40°. Further elevation of the temperature lowers the current efficiency for permanganate and increases the quantity of slime formed.

[5] To obtain manganate by electrolysis in concentrated NaOH it is recommended that the anode c.d. should be between 2-5 A/dm^2. To obtain sodium permanganate by electrolysis of Na_2CO_3 optimum results were obtained at c.d's. of 5-10 A/dm^2.

[6] Decrease of the surface area of the cathode relative to that of the anode in an electrolyte containing caustic soda increased the current efficiency for manganate. With carbonate solutions and formation of permanganate, change of the ratio of surface areas of cathode to anode did not have much effect.

[7] A small increase of current yield for manganate and permanganate was observed when the electrolyte was stirred, and when the distance between the electrodes was increased.

[8] To obtain sodium and potassium manganates and permanganates by anodic solution in alkali, not only may plates of electrolytic manganese be used, but also castings obtained by fusion of electrolytic manganese.

[9] It is possible to obtain $NaMnO_4$ and Na_2MnO_4 by electrolytic solution of metallic manganese with an energy consumption of 4-6 kw-hr/kg Na_2MnO_4 in NaOH solutions and 20 kw-hr/kg $NaMnO_4$ in solutions of Na_2CO_3 with a product yield for manganate of 80-95% and a current efficiency of 30-58% for solutions of NaOH and 20-32% for solutions of Na_2CO_3.

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MECHANISM OF GROWTH OF CRYSTALS OF SODIUM BICARBONATE [1)]

Ya. R. Goldshtein

The main aim in the process of carbonation of ammoniacal liquors is to obtain sodium bicarbonate crystals of definite size and form, easily filtered and washed free of the mother liquor. In previous communication [1], the process of crystallization was examined from the point of view of its kinetics, leaving aside its relation to the properties of the crystals obtained. The present communication is devoted to the elucidation of the means of obtaining bicarbonate having the desired properties.

Carbonation columns are the seat of rather intense action, and crystallization proceeds in them at a considerable rate. From the point of view of the production of crystals at a definite rate, what should be known is the quantity of substance which can separate from the given solution in unit time under conditions which guarantee the formation of crystals of specified size and shape. In order to secure regular and rapid crystallization, it is necessary to investigate the kinetics and the mechanism of growth of bicarbonate crystals. It should be observed that determination of the course of a crystallization by calculation, based on the assumption that growth occurs simply from a number of initially formed crystallization centers, is not possible, as is also the case in the majority of technical processes, because the basic factor in the growth of crystals is, as is shown below, the clustering together of individual crystals.

EXPERIMENTAL

Influence of the supersaturation on the size of the crystals. In the previous communication [1] data about the kinetics of the development and elimination of supersaturation were reported. Together with the extent of the supersaturation, the size of crystals of bicarbonate was observed in parallel experiments by means of a microscope with a magnification of 160. The size of the crystals was measured with an ocular micrometer.

In Fig.1 are set forth some more characteristic forms of crystals of sodium bicarbonate, observed both under laboratory and plant conditions. As a rule the bicarbonate crystals formed are spindle-shaped and are tapered at both ends (a). In carbonation towers such crystals are rarely met with, and only in the initial stages of crystallization. They predominate in towers producing purified bicarbonate and approach large dimensions (150-200μ). After the beginning of massive crystallization under laboratory conditions, long prismatic crystals with blunt ends are observed. (b). They are frequently met with in plant towers. The width (diameter) of such crystals grows continuously during carbonation, and they gradually convert into the so-called "barrels" (c). The larger these "barrels", and the smaller the number of crystals of the other form and of fine crystals, the "better" the bicarbonate from the industrial point of view. Very large crystals, however, are also undesirable, as they behave worse on filtration. The width of the "barrels" is about equal to their height.

"Sheaves" of crystals are frequently observed, heavy in the middle (d), and still more frequently nodules (e) - stellate aggregates of crystals. Very fine

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1) Communication III on the Study of the Theory and Practice of the Ammonia-Soda Process.

crystals (usually acicular) form aggregates of indeterminate shape - flocs, which we term "aggregated fines" or just "fines".

In Table 1 are shown the characteristics of crystals obtained in experiments reported in Table 6 of the previous paper [1]. In these experiments carbonation proceeded for only ten minutes after the start of intensive crystallization (after the "appearance of turbidity"). It can be seen from the third column of the table that in this period 6-30 n.d. of bicarbonate was precipitated. We recall that the total quantity of bicarbonate precipitated by carrying the reaction right to the end is 68-73 n.d. (1 Normal Division = 1/20 g.-equiv.).

In the fourth column of the table is given the change of the extent of supersaturation in the course of ten minutes carbonation after the appearance of turbidity [1]. The (+) sign indicates an increase, and the (-) sign a decrease, in the supersaturation in this period. This column demonstrates the close connection between the dynamics of the change of supersaturation with the size of the crystals. Coarse crystals were obtained only when the supersaturation increased during crystallization; when it fell, they were small. This is explained by the fact that the degree of supersaturation after the initiation of crystallization increases only at small rates of carbonation, while crystallization starts (but very slowly) at a small degree of supersaturation. The larger the degree of supersaturation at the moment of commencement of crystallization, the more rapid is the latter and the greater the fall of supersaturation in ten minutes. It is clear that in this case, as was also shown by observation, a larger number of crystallization centers and a poorer growth of crystals is obtained.

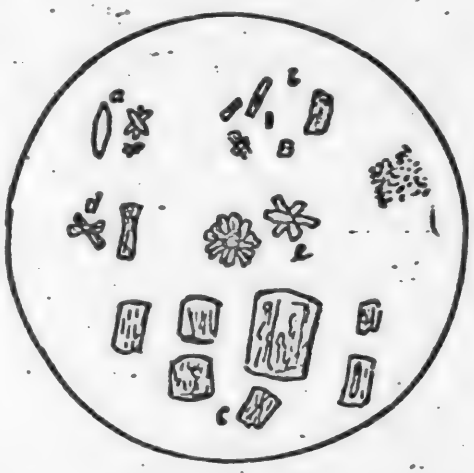

Fig. 1. Typical forms of sodium bicarbonate crystals. See text for description.

TABLE 1

Influence of Rate of Carbonation and Temperature on the Size of Crystals

Temperature (°C)	Rate of carbonation (liters of CO_2/min)	$NaHCO_3$ pptd., in n.d.	Change in supersaturation in 10 mins.	Character of crystals
30	0.2	6.0	+ 5.4	70-85μ, a large part of them nodules
30	0.5	15.4	- 4.1	Fines and crystals overgrown with fines
30	1.0	29.8	- 9.9	Fines in aggregates of 85-120μ
45	0.2	6.6	+ 8.7	Crystals of 70-95μ
45	0.5	16.7	- 1.3	Crystals overgrown with fines
45	1.0	26.5	- 7.9	Aggregate fines
60	0.2	9.4	+ 2.5	Crystals of 120-140μ
60	0.5	18.6	- 1.2	ditto
60	1.0	25.6	- 5.6	Groups of crystals 25-80μ, falling into fines

The supersaturation, determined by our method, is the sum of the crystallizational and the "reaction" supersaturation - the latter covering the conversion of ammonium carbamate to carbonate. The equilibrium between carbamate and carbonate is continuously displaced towards a decrease in the ratio $M = \frac{\text{carbamate } CO_2}{\text{total } CO_2}$; The conversion goes slowly right up to the critical point (110% carbonation) at which both the rate of attainment of equilibrium and the rate of its displacement increase sharply.

In order to get the minimum number of seeds it is necessary to carbonate at such a rate that up to the critical point: 1) the crystallizational supersaturation accumulates to an extent sufficient to start crystallization after a short induction period, and 2) a sufficient quantity of bicarbonate crystals (seeds) separates. In this case the rapid formation of bicarbonate at the critical point cannot create such a dangerous crystallizational supersaturation, at which the rate of separation of bicarbonate exceeds the quantity which can be crystallized onto the crystals which have already separated out earlier.

The growth of supersaturation observed by us after the initiation of crystallization is related, apparently, not to the crystallizational supersaturation, but to the accumulation of an excess of carbamate above the equilibrium quantity. The conversion of this excess carbamate to carbonate and the subsequent exchange reaction (metathesis) involving the formation of sodium bicarbonate always continues after the withdrawal of the sample.

The true crystallizational supersaturation at the moment of withdrawing the sample may be determined by a short period of intense stirring of the sample with a large quantity of seed crystals. Separate experiments of this nature, reported in the previous paper[1], showed that the true crystallizational supersaturation usually does not exceed 6-8 n.d.

If the process of carbonation is conducted at such an intensity that spontaneous crystallization only starts at the moment the critical point is attained, i.e., when the supersaturation is of the order of 18-25 n.d., then the crystallization proceeds at an enormous rate, resulting in the formation of many fine crystals.

The experimental data set out above permit the quantitative fixing of the limiting permissible rates of carbonation at the initiation of crystallization.

Table 1 refutes the frequently expressed opinion that at lower temperatures poor crystals are bound to be formed. Coarse crystals can be obtained at any temperature by advancing the normal rate of crystallization (carbonation). At a carbonation rate of 0.2 liter/min, coarse crystals were obtained at all three temperatures, although only 3-8 n.d of bicarbonate were precipitated. The number of initial centers was, consequently, very small and, we may add, though this is demonstrated better below, the conditions of carbonation favor the adherence of crystals to one another.

At a rate of carbonation of 0.5 liter of CO_2/min, quite satisfactory crystals were obtained only at 60°. At 45°, side by side with relatively large crystals there were also fines, and at 30° fines predominated. The quantity of bicarbonate precipitated was equal to 15-18 n.d.

At the maximum rate of carbonation of 1 liter/min, only fines were formed at 30 and 45°, while at 60° there were small crystals and fines. The length of the fine crystals was 2-3μ, the width about 1μ . These crystals in small

quantity stick to large crystals, giving brushlike forms, which are also formed in larger quantity by independent accumulation.

All the crystals with the exception of the fines were prismatic, with blunt ends.

In the laboratory tower with disc nozzles carbonation was conducted at still higher rates (3 liters of CO_2 per min). In this case for example at 30° during the period of precipitating 30 n.d. bicarbonate, only fine crystals of length 2-4 μ were obtained. Such a deposit, even after dehydrating with alcoho still stuck together in clumps. At 45° also many such fine crystals were obtained, but a part of the crystals attained a size of 20 μ. At 60° the deposit was friable, the size of the crystals 55-60 μ. Consequently, coarse crystals may be obtained without difficulty at rates exceeding those attained in industrial carbonation towers.

The data reported permit the rough calculation of the permissible rate of crystallization of bicarbonate during the initial period of its precipitation: at 30° it is 0.7 n.d/min, at 45° 1 - 1.2 n.d./min, and at 60° it is 1.8 n.d.

Effect of stirring on the growth of crystals. As in the experiments described above, and in those in plant columns, stirring of the suspension during the time of reaction is achieved by brisk circulation of the gas. When the quantity of gas passed per unit time increases, not only is the carbonation accelerated, but also the suspension is better stirred.

To elucidate separately the role of mixing, separate experiments were carried out in a vessel with a frame stirrer. It was shown that at 200 rpm only fine acicular crystals were obtained even at the minimum rate of carbonation of 0.2 liter/min at 30° and 0.5 liter/min at 60°. Consequently, intensive stirring prevents the formation of coarse crystals. We shall return to this question later.

Introduction of seed crystals as a method of studying the process of crystallization. The possibility of diminishing the quantity of crystallization centers, formed during the initial period, by introducing "seeds" is generally known. Their application to the ammonia-soda process was studied by Pavlov and Dubrovina.

This work showed that there is a definite positive effect of seeds (bicarbonate crystals) on the quality of the crystals obtained, but neither the quantitative aspects of this phenomenon, nor its mechanism, nor the practical form of its utilization were worked out.

Instead of the term "seeds" which usually refers to individual crystals, introduced into strongly supersaturated solutions to create spontaneous crystallization in it, we would prefer to use the more correct term, "crystallization supports," because the mode of action of the crystals introduced is basically as supports on which the crystallization occurs.

The answer to the question as to whether in general crystal supports are necessary for the production of coarse crystals, provided by the experiments described above as well as by general plant experience, is in the negative. In our investigations crystal supports have been widely used, but this has been done not as an end in itself, but as a method of studying the process of crystallization and of determining the rate of growth of crystals of bicarbonate.

In the course of carbonation the amount of precipitated bicarbonate continuously increases. In parallel with this, due to the fall in the pH of the solution, there is a fall in the rate of absorption of CO_2, and consequently in the rate of precipitation of bicarbonate. The conditions of crystallization continuously change

for the better. The conditions of experiment should exclude the effect of these changes. In experiments described and reported below, the following factors were changed: the rate of formation of bicarbonate, the temperature and the quantity of the crystal supports.

The rate of formation of bicarbonate may be changed in three ways: a) by changing the rate at which CO_2 is passed through the solution, i.e., by changing the absorbing surface; b) by changing the surface of absorption by changing the diffusers, the form of the vessel, etc; and c) by utilizing the fall in the rate of absorption with the progress of the operation itself - change in the pH of the solution. Within the experimental limits we utilized the first method and in part the second. In the given case they were useless, because they changed the conditions of agitation which affected the growth of crystals. Hence the third method was used. For the experiments solutions were used, previously carbonated to different pH's (i.e. different degrees of carbonation) and the precipitate of bicarbonate separated from them after standing for two days. The composition of the solution in the tables is characterized by the quantity of combined ammonia (equivalent to the bicarbonate precipitated). A solution with 0 n.d. corresponds to 82% carbonation.

The carbonation was carried out in glass tubes of diameter 30 mm, passing CO_2 through at 1.1 liter/min. Samples of the deposit were filtered off immediately after interrupting the carbonation, a micro vacuum filter being used for this purpose: the crystals were washed in succession with saturated bicarbonate, alcohol and ether.

As a crystal support coarse, uniform, spindle shaped crystals taken from columns working on technically purified bicarbonate were employed, about 150 μ long.

The basic objective of the experiments was to find out, by systematically increasing the amount of support crystals, the minimum quantity of them at which all the crystallized bicarbonate crystallized on the supports, and no new centers of crystallization were formed.

The experimental data is set out in Table 2. By comparing the first and second columns of the table the quantity of bicarbonate can be seen, and the 7th column gives the amount of supersaturation accumulated during the same period of time. The duration of the process of crystallization reported in the 4th column permits a calculation of the actual rate of crystallization of bicarbonate, which is given in the 8th column.

Table 2 shows that for any temperature such a quantity of supports may be selected as will make crystallization at high rates possible without the formation of new centers of crystallization. Neglecting experiments in which fine crystals were formed, the rate of crystallization at a given temperature, in which the only process is the growth of the supports introduced, can be established. It should be observed that, by diminishing the size of the support crystals, a smaller weight can be employed, because what is of importance is their surface and not their actual weight. The surface of the crystals increases in inverse proportion to their equivalent radius.

In a number of cases, increase of the quantity of supports increases the rate of absorption. This is particularly clear at 45 and 60°. It is evident that, by accelerating the dispersal of the supersaturation, increasing the amount of support crystals ensures the separation of HCO_3^- ions from the solution, which simultaneously raises the pH of the solution and its absorptive capacity.

At 45°, even at the rate of crystallization of 1.3 n.d., no difficulty is

TABLE 2

Role of Quantity of Support Crystals

Quantity of bound ammonia			Duration of experiment (in minutes)	Quantity of support crystals	$NaHCO_3$ pptd. (in n.d.)	Supersaturation (in n.d	$NaHCO_3$ pptd./min	Properties of crystals
in the initial solution	after the experiment	after elimination of supersaturation.						
			Temperature 30°					
0	14.0	24.6	20	40	14.0	10.6	0.7	Support crystals covered by fines
0	12.0	19.3	20	50	12.0	7.3	0.6	Support crystals increased in size
21.6	28.0	38.4	15	5	6.4	10.4	0.43	Support crystals covered by fines.
24.6	28.0	36.8	15	10	6.4	8.8	0.43	A few fines
16.4	23.6	34.0	15	20	7.2	10.4	0.48	No fines
16.4	23.6	31.6	15	40	6.0	9.2	0.40	ditto
34.4	46.8	51.0	30	5	12.4	4.2	0.41	A few fines
34.4	46.0	51.4	30	10	11.6	5.4	0.38	No fines
49.8	52.8	55.8	15	5	3.0	3	0.20	ditto
			Temperature 45°					
0	36.4	41.0	30	10	36.2	4.6	1.2	Supports covered by fines
0	38.0	41.6	30	20	37.8	3.6	1.26	A few fines
0	38.0	41.6	30	30	40.0		1.33	No fines
21.2	30.4	38.4	15	5	8.2	9.0	0.53	Fines precipitated
21.2	30.4	36.8	15	10	8.2	7.4	0.53	
16.0	46.0	49.6	30	10	30.0	3.6	1.0	Only coarse support crystals
30.0	32.8	37.4	30	0	2.8	7.4	0.09	
30.0	35.2	38.4	30	5	5.2	3.2	0.17	
			Temperature 60°					
0	36.0	38.4	30	5	32.6	2.4	1.08	Did not succeed in growing fine crystals
0	32.0	35.0	30	10	28.6	3.0	0.95	
0	37.6	38.8	30	20	34.2	1.2	1.14	
21.6	27.8	33.0	15	5	6.2	5.2	0.8	No fines
21.6	31.8	35.9	4	20	10.4	5.1	0.69	

encountered in getting large crystals. At 60° the task is so much easier that it is not necessary even to prescribe a limiting rate of crystallization in the presence of support crystals.

From the data of Table 2 the minimum quantity of crystal supports necessary to prevent the formation of new crystallization centers at different temperatures and rates of crystallization can be calculated. The results of these calculations are set forth in Table 3.

The data of Table 3 have been utilized for the construction of diagrams (Fig. 2).

TABLE 3

Minimum Quantity of Support Crystals, Necessary to Prevent the Formation of New Centers of Crystallization

Temperature (in °C)	Rate of crystallization of $NaBCO_3$ (in n.d/min)	Quantity of supports	Quantity of bound ammonia in initial solution	Duration of carbonation (in min)	Final supersaturation (in n.d.)
30	0.6	50	0	20	7.3
	0.48	20	16.4	15	10.4
	0.43	10	21.6	15	8.8
	0.38	10	34.4	30	5.4
	0.20	5	49.8	15	3.0
45	1.3	30	0	30	-
	0.53	10	21.2	15	7.4
	0.17	5	30	30	3.2
60	0.95	10	0	30	3.0
	1.14	20	0	30	1.2
	0.8	5	21.6	15	5.2
	0.75	0	0	30	7.8

On the ordinate axis are plotted the bound ammonia contents (NH_4Cl) in the initial solution subjected to carbonation, while the other axis is divided in units of quantity of support crystals. The method of using the diagram is best illustrated by the following example. If we have a solution with 20 n.d. bound ammonia, then the deposit will likewise contain 20 n.d. sodium bicarbonate (in the course of the carbonation of an ammoniacal liquor). This quantity of bicarbonate as supports is not sufficient to prevent the separation of fines at 30°. In order to find the quantity of supports necessary and consequently also the amount of bound ammonia, (so long as supports are not introduced from outside, these quantities are always equivalent, a point on the 30° curve, must be so located that the perpendiculars drawn from it to the abscissa and ordinate axis cut off equal intercepts on both. These intercepts indicate the degree of carbonation of the solution, above which there will be no further formation of new centers of crystallization. At 30° this is 22.5 n.d. bound ammonia, at 45° and at 60° approximately 5 n.d. bound ammonia.

The region to the left of the curves is that in which the carbonation always involves the formation of new centers, while the part to the right of the curves is the zone in which all the bicarbonate precipitated grows on the crystals already present in the solution.

In our experiments the crystallization (carbonation) went on for example at the same velocity as the average rate in plant columns, hence the data may be directly used for industrial calculations. It should be

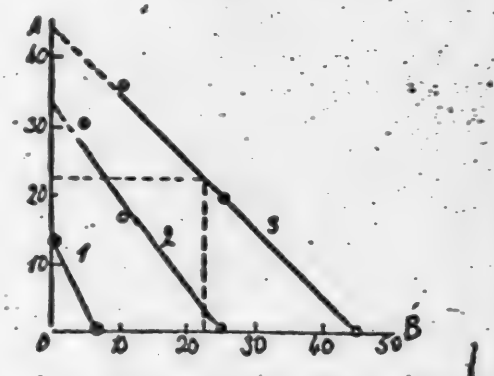

Fig. 2. Quantity of crystal supports requisite to prevent the formation of new centers of crystallization. A - Quantity of NH_4Cl in the initial solution (in n.d.); B - quantity of supports (in n.d.). 1 - 30°, 2 - 45°, 3 - 60°.

borne in mind that the support crystals in our experiments were coarse. In plant columns the crystals grow continuously and at the begining somewhat fewer supports are required than are given by calculation, and at the end somewhat more. Our data cannot therefore be taken as absolutely accurate, but we cannot say how exact they are because, as we shall see below, the rate of carbonation in industrial columns is not constant, because of the continuous change in the CO_2 partial pressure. The accuracy of all these figures is sufficient for industrial needs.

Average rate of growth of the boundaries of bicarbonate crystals. A number of conclusions can be drawn from our results, and in particular, the average linear rate of growth of the crystal boundaries at different temperatures at 6-8 n.d. can be calculated. For this certain assumptions must be made.

With dimensions of the spindle shaped crystals as 150μ in length and 80μ in maximum width, the surface of 1 n.d. of supports can be roughly calculated in the following manner. The surface of one crystal is $6.1 \cdot 10^4 \mu^2$. The volume of one crystal is $9.6\ 10^5 \mu^3$ and the weight $\frac{1.16 \cdot 9.6 \cdot 10^5}{10^{12}} = 2.07 \cdot 10^{-6}$ g. 1 n.d. of bicarbonate corresponds to 4.2 g and therefore contains $2.03 \cdot 10^8$ crystals, having a total surface of $12.1 \cdot 10^{10} \mu^2$, or 1210 cm^2.

From the data of Table 3 it follows that at 30° in the presence of 10 n.d. supports, crystallization can occur at 0.4 n.d./min. 0.4 n.d. has the volume of $\frac{0.4 \cdot 4.2}{2.16} = 0.78$ cm^3. Hence the average linear rate of growth of the crystal boundaries of sodium bicarbonate will be 0.78: 12100 = $6.4 \cdot 10^{-5}$, or 0.64μ/min. In this way we find at 45° a rate of growth of 0.85μ, and at 60° one of 2.0μ/min. These are minimum rates: they can possibly be larger, but with the risk of formation of new crystallization centers.

The rate of growth of the separate boundaries of the crystals is different. They grow more rapidly in a longitudinal than in a transverse direction. Hence at 60° the axial rate of growth of the crystals is not less then 6-8μ/min, (counting the rate of growth of both sides). Our observations showed that, in practice, in the initial period of slow crystallization the spindle shaped crystals grow axially by 80 μ i.e. a rate of growth of 10-12μ/minute. Taking into account the arbitrary nature of a number of our assumptions, the agreement between the results may be taken as completely satisfactory.

Limiting intensity of crystallization in carbonation towers. The crystallization in carbonation towers begins at 60°. At this temperature, and at a rate of formation of 0.75 n.d./min, crystal supports are quite unnecessary as follows from Table 2. In plant columns the zone of high temperature occupies a length of 4.4 meters.

In this zone 28 n.d. bicarbonate actually comes down. Calculation shows that the time of residence of the liquor in this zone is 30-40 minutes. The average rate of crystallization is therefore 0.7 n.d./min, i.e. it is less than the permissible.

At 45° it is necessary to have 30 n.d. of supports, in order to crystallize at 1.3 n.d./min. In the upper "cold pans" such a rate is occasionally exceeded, and is usually 0.9 - 1.3 n.d./min, as is evident from the "photographs" of the working of towers [1]

At 30 n.d., in the presence of 50 n.d. supports, bicarbonate may be crystallized at 0.6 n.d./min. In the zone whose temperature is near (slightly higher than) 30°, there is always such a quantity of supports present.

In this way the minimum residence time of the liquor in various parts of the column, i.e., the productivity of the latter, may be calculated (Table 4).

57 minutes are required in toto for the crystallization of 70 n.d.

In the second column of Table 4 are given the quantities of bicarbonate, separated from the beginning of the carbonation. As follows from the table, it is necessary to carry on crystallization to completion in about an hour, in order not to allow the formation of any fines in any of the zones (not counting, of course, the first moments of crystallization at 60°). In the calculation it is assumed that the time of residence of the liquor in each zone is completely and properly used for crystallization, i.e. that in each zone no less bicarbonate comes down, than would be expected from the table. As is shown below, it is extremely difficult to get such uniform or regular precipitation in plant columns (and indeed in laboratory ones as well). The trouble is not that of carrying on the crystallization at such a rate but, on the contrary, of restricting the rate of absorption of CO_2 exactly to the definite level. A particularly dangerous zone is that at the beginning of cooling 60-45°, where the equilibrium is strongly displaced, and therefore the reaction is accelerated.

TABLE 4

Minimum Duration of the Process of Crystallization in Separate Parts of the Column

Temperature of zone		Bicarbonate formed (in n.d.)		Permissible rate of crystallization (n.d./min)	Duration of crystallization (in minutes)
From	To	From	To		
60	60	0	10	0.75	7.5
60	60	10	30	1.0	12.5
60	45	30	55	1.3	19
45	30	55	70	0.6	18

In practice we need to have a considerable reserve of residence time in a column: for the hot zone 10-20% is sufficient, for the 60-45° zone 30-40% reserve must be available, and for the lower zone it must be 20-25%. 70 minutes in general suffices to cover this crystallizational time reserve. If it is considered that crystallization does not commence in the upper part of the column, the time of residence of the liquid in the column is calculated to be 85 minutes. In practice the duration of carbonation is 35-100% longer, but columns are repeatedly used at loads corresponding to a carbonation period of 1.3 hours, and yield satisfactory bicarbonate. However when used at such loads the columns are clearly at the limit (for crystallization), and give reduced yields (coefficient of utilization of the sodium). With intensive cooling, which is necessary to obtain a normal sodium utilization coefficient, the columns easily crystallize: bicarbonate separates not only on the support crystals but also on the walls of the tower and fines are formed as well, which impedes the flow of the solution – the tower is said to "choke".

Growth of crystals of bicarbonate in the towers. It is frequently assumed that the final size of the crystals is determined by the relation between the quantity of crystallization centers formed in the initial stages of the process, and the total quantity of crystallizing substance, i.e. by the material available for growth on the centers. In this case the decisive factor would be the initial degree of supersaturation.

To test this we made above 20 observations on the change in the character and size of crystals in going down a column. In the zone where precipitation of bicarbonate commences, the crystals are usually spindle shaped but extremely fine, gradually growing to a maximum length of 10μ. In this zone the first 10-12 n.d. of bicarbonate comes down. Below this, in the hot zone, we observed crystals growing to 25-35μ in length, and still lower, at the 9th pan, the crystals reached 50-70μ in length. All of these were prisms with blunt ends.

In the suspension at the 7th pan (where intensive cooling of the liquid occurs) a sharp growth of the size of crystals to 60-100μ is observed but alongside this a fresh precipitation of fines is frequently observed. Later on the large crystals do not grow much, but the fines gradually disapper, and defects of the large crystals close up. A mixture of different forms of crystals emerged from the tower, but with "good" bicarbonate there is a predominance of the "barrel" type of crystal, whose size is 90-100μ on the average. Where the cooling is intense many "nodules" and general concretions are to be seen.

An extremely simple calculation is sufficient to convince one that it is not possible to assume that the only process in the tower is the simple growth of crystals.

If it is assumed that the crystals formed after the precipitation of the first 8 n.d. of bicarbonate, are 20μ long, which is known to be an exaggeration, then their equivalent diameter would not be more than 7μ.

Crystals obtained from the towers have an equivalent diameter of 90μ. The mass of the latter would be $(90:7)^3 = 2120$ times that of the small initial crystals. Hence in order for 20 n.d. of bicarbonate of mean diameter 20μ to grow to 90μ, it would be necessary for not less than $8 \cdot 2120 = 17$ n.d. of bicarbonate to crystallize out. In actual fact only 60 n.d. separates out, which is 17,000:60 = 283 times smaller. Consequently, for 283 crystals existing in the hot zone, only one crystal is formed.

Crystals can disappear only as a result of agglomeration with other crystals. Whether they dissolve and later recrystallize cannot be said, because the size of 20μ which we took for our calculation was sufficiently large. In reality examination of the crystals clearly shows them to be polycrystalline, concretions of different types. They adhere mainly along the long axis, but partly in stellate clusters - nodules - to which type the "sheaves" also belong. On the average the spindle shaped crystals were not observed in the lower parts of the towers.

Concretion of crystals, as a basic form of growth. Its mechanism. We studied the separate forms of aggregation of crystals during the production of soda. Crystals of calcium carbonate in previously purified liquor aggregated mainly by the formation of loose junctions between separate small crystals of $CaCO_3$ and also by their flocculating by finely dispersed particles of magnesium hydroxide. In the process of purifying liquors by absorption, the crystals of calcium carbonate cement together in dense aggregates by the precipitation on their surfaces of the triple salt nortupite: $MgCO_3 \cdot Na_2CO_3 \cdot NaCl$. The aggregations of calcium carbonate also occur during the causticizing of soda by lime. Such clustering plays a large part in industry, and facilitates the breaking of suspensions.

Such phenomena also occur in the case of bicarbonate. Seeds of bicarbonate, formed by spontaneous crystallization, rapidly grow into spindle shaped crystallites. Side by side with this growth, they become aggregated together as a

result of collision. Such aggregations are loose, because the crystals only adhere at certain points along their boundaries. The larger the surface of contact, the more compact is the aggregate. Since the side faces of the crystals have a considerably larger surface than the other faces, the crystals adhere predominantly along their long axes.

The period of residence of 2 crystals in contact depends on the intensity of agitation. Convection and other currents in the liquid, caused by the passage of gas through it are incident upon the clusters of crystals at different angles and with different intensity, and tend to separate the crystals from one another. During the short time in which the crystals are in contact, precipitation of bicarbonate on them continues. As a result of this there are formed on the free surfaces of the crystals, at those parts where they are in contact, "seams" of bicarbonate, or more correctly single layers of bicarbonate, joining both surfaces together. As a result loose junctions are turned into compact clusters.

The weaker the agitation, the longer the time in which crystals are found in contact and so much the larger is the thickness of the layer that can be formed. For the aggregation of two large crystals naturally a thicker layer is necessary, than for welding two fine ones together. Hence when the agitation is intense, only a few aggregates can be formed, and when the agitation is specially intense, clustering is in general impossible.

The second factor, limiting the intensity of aggregation, is the rate of separation of bicarbonate from solution. The more rapidly this occurs, the thicker the layer formed in unit time. With a high rate of precipitation of bicarbonate, clustering of crystals in abnormal positions is possible, for example crosswise, ("nodules") and they can attain larger sizes than usual. The mother liquor can only be washed out with difficulty from the narrow fissures between the crystals in such nodules.

The thickness of the junction, however, is not determined only by the rate of separation of the bicarbonate. The surface on which this separation occurs must be known. When there is a large surface of crystals (supports) the material separating on it is spread out in a thin layer. It is known that the conditions at the start of crystallization favor clustering. In practice, however, the surface of the crystals present cannot grow by clustering but diminishes, and that very considerably, as can be seen from the calculation given above. Hence in towers thick junctions, conditioned by the separation of a definite quantity of bicarbonate, grow continuously and the conditions for clustering improve towards the bottom of the towers.

Clustering does not go on without limit. The strength of the bond between two crystals relative to their combined mass decreases as the crystals grow. The ability of agitation to separate clusters increases as they grow, because the surface on each crystal exposed to the action of the current in the liquid increases unequally on each side. The agitation must be decreased in intensity. In order for crystals to remain in suspension, however, a definite minimum intensity of agitation is necessary. If the crystals fall to the floor of the vessel, collisions between them are terminated, and consequently their clustering ceases also (on the floor of the vessel clustering of the crystals into a single aggregate can occur, but this is a negative effect). The limiting size of the polycrystal is set, therefore, by the intensity of the agitation which is necessary to keep it suspended.

Since the intensity of the agitation is determined by the amount of gas passing through, the size of the crystals should decrease with increase in the load on the tower (i.e. with its output). At a given output of the tower the

size of the crystals should be directly proportional to the concentration of the gas. And actually, in one of our plants, by obtaining concentrated waste gas and feeding the column with gas containing 65% CO_2 instead of 40-45% which is usual for these plants, course "barrels" were obtained, which were wider than they were long. The limiting size of the polycrystal varied between 100 and 120μ.

Let us examine a concrete case of growth of crystals in a tower from the point of view of our assumptions about the mechanism of growth. In the first stage of the carbonation the liquor is heated to 55-60°. The formation of bicarbonate can begin only after heating the liquid (completion of monocarbonation). At this point partial pressure of CO_2 in the tower is small - about 0.5 atm, and at the temperature given the system is very near to equilibrium. The absorption of CO_2, and consequently the formation of bicarbonate as well, is extremely slow (there are frequent cases when the absorption of CO_2 simply does not occur at all over the whole extent of some pans). This forestalls the accumulation of any considerable degree of supersaturation, as was shown in detail in our previous communication [1]. The crystallization begins quietly, favored by the discarding of crystals from the lower pans, thanks to the agitating action of the gas. Spindle shaped crystals are formed, growing fairly rapidly. When the rate of separation of bicarbonate is small, the process of clustering is not very intense, hence we frequently observe spindle shaped mono-crystals in the initial zone of crystallization. Quickly, however, thanks to increase in the partial pressure of the CO_2 in the lower part of the column the separation of bicarbonate gains in strength and as a result of the intense axial clustering the spindle shaped crystals disappear, being transformed into long prisms. Traces of clustering were observed in the form of serrated ends (Fig. 1). The lateral surfaces were observed to have a tendency to straighten out. With the rapid growth of the crystals the formation of spindle shaped planes is not possible, hence it is not always possible to discover spindle shaped crystallites in the tower even at the point where crystallization commences.

At higher temperatures the true growth of the crystals is higher (cf, the figures quoted above) and the rate of clustering together becomes extremely large. Hence in the hot zone the growth and clustering of polycrystals is extremely fast and in the lower parts we meet with fairly coarse crystals, size up to 100μ alongside small crystallites.

A completely different picture is presented by crystals from towers operating on technically pure bicarbonate, in which ammonia-free soda solutions are carbonated. Though the behavior of such towers at different heights was not investigated, nevertheless a view of the final crystals shows without doubt that the basic process in such towers is the growth and not the clustering together of crystals. As a rule they are of the spindle form. The crystallization temperature in these columns reaches 75-80°. The crystallization proceeds uniformly at all heights and at an average rate 2-3 times less than in the normal carbonation columns. The intensity of agitation of the bicarbonate columns is high, because they operate on dilute flue gases, the coefficient of utilization of which is not great. High alkalinity of the solution (in which there is always an excess of Na_2CO_3) accelerates the growth of crystals. The combination of all these factors produces these spindle shaped crystals at the start of the crystallization, and causes them to grow normally. Also the growing spindle shaped crystals cannot easily adhere to one another, thanks to convex form of the lateral faces.

From the results presented in communication II [1] it emerges that in the initial stages of crystallization in ammonia solutions coarse spindle shaped crystals are formed, and this shows that the form of the crystals depends not on the composition of the solution, but only on the kinetics of separation of material from it.

With the beginning of cooling in the tower (without this cooling the reaction ceases) the absorption of CO_2 increases sharply, and the separation of bicarbonate then increases sharply also. The temperature in this zone is still sufficient for junctions to be formed rapidly. It is in this part that coarse stellate clusters are easily formed because the compact junctions between the crystals promote growth, even when the crystals are associated in abnormal positions. In this zone the width and, to a lesser degree, the length of the crystals increases rapidly. The width of the barrels, however, is still small. They grow gradually as the cooling of the liquid proceeds, at the expense of the addition of finer crystals to the coarse ones and by the bridging over of cavities formed by clustering with simultaneous overgrowing of all surfaces. As a result a considerable proportion of the defects of the clustered forms are healed, and the majority of nodules acquire normal outlines also. None the less, as can be seen from Fig. 1, traces of growth can be seen on nearly all crystals; they are shown by cavities, jagged ends ("bottoms" of the barrels). There are many evidences of clustering in the lower parts of the towers.

In Table 5 are set out data from a systematic study of the dynamics of growth of crystals as a function of the height of the tower. The observations were made in the course of the whole period of operation of a tower, from one flush to the next, i.e. about 4 days.

In the columns headed "apparent volume" the results of determinations of the quality of the bicarbonate from the volume of the precipitate are given. The figures are the volumes, (in percentages), occupied by 68 n.d. bicarbonate after settling of the suspension. Rough observations of this kind have been used for a long time in industry. The figure of 68 n.d. is chosen because it is near to the normal content of bicarbonate in the liquid in a tower. In the column headed "volumetric weight" are given the figures of the preceeding column (apparent volume) recalculated on the more usual basis of the volume occupied by 1 g of deposit (in ml). The method of determining the apparent volume as an index of the quality of the bicarbonate is given in our paper [2].

The 8th pan is directly over the first cold pan (in general No. 7 is taken as the one below it). The liquid in it has already cooled to 50-57°, so that fines are easily formed, as noted in the teble. No. 4 pan is in the middle of the cold zone. The collectors are the vessels from which the liquid is withdrawn for filtration. From the table it can be seen that the apparent volume of the precipitate from the 8th pan always exceeds 100, and on the 4th day of working reaches 400. This means that, if all the bicarbonates were of such a size that none of it could settle out, we should observe a thick "porridge" of crystals. This is a hypothetical case, but the conversion of the solution to a gruel-like mass is always observed in carbonation towers on cooling. By shaking vigorously a certain quantity of liquid can be extracted, but on standing once again the crystal mass imbibes the liquid.

The suspension in the 4th pan contains usually only a small quantity of fines. Only at the end of the period of working of the tower does the quantity of fine crystals increase so much, that they form independent aggregates. The deterioration of the quality of the crystals as the working of the tower pro-

ceeds is explained by crystallizing on the surfaces of the cold tubes. Thanks to this more water is given out on cooling, and the uniformity of cooling as a function of height is lost, the temperature gradient becoming sharper at the beginning of the cooling zone.

TABLE 5

Dynamics of Growth of Crystals of Bicarbonate as a Function of the height of the Tower

No. of pan and collector[1]	Day and hour[2]	$NaHCO_3$ pptd. (in n.d.)	Apparent volume	Volumetric weight	Microscopic characteristics
8	I, 10	26	156	0.15	35-60μ, overgrown with fines, "barrels"
	I, 11	25	109	0.26	45-60μ, overgrown with fines
	I, 13	26	178	0.16	Ditto, accompanied by aggregated fines
	III, 11	28	140	0.21	Overgrown crystals and aggregated fines
	III, 13	27	205	0.13	Large accumulation of fines and separate crystals
	IV, 8	28	203	0.14	Accumulation of fines and 60-90μ crystals
	V, 8	23	467	0.06	Aggregate fines
4	I, 10	49	68	0.42	80-90μ, very few fine
	I, 11	47	57	0.50	Ditto
	I, 13	52	62	0.46	Ditto, with "barrels" of up to 130μ
	III, 11	48	85	0.34	50-60μ rarely 90-120μ
	IV, 8	51	108	0.20	
	IV, 14	47	175	0.16	Separate crystals and accumulated fines
	V, 7	48	96	0.30	Crystals of 60-70μ and accumulated fines
1	I, 10	60	42	0.68	Crystals of 100-120μ, together with fines
	I, 11	64	44	0.65	Ditto
	III, 11	65	38	0.75	Average quality, usually 80-100μ
	III, 13	66	41	0.70	90-120μ, many 40-60μ
	IV, 8	67	41	0.70	Ditto
	IV, 14	65	42	0.68	Ditto
	V, 7	67	48	0.60	"Nodules" of 45-60μ, no coarse crystals (above 90μ)

On leaving the column (through the collectors) the apparent volume becomes more constant. The crystals are usually seen to be a mixture of all sizes and shapes, and the differences result in a change of the proportion of the separate fractions. The characteristic size distribution for bicarbonate below the average quality is: 80-120μ and higher 26%; 50-80μ 42%; less than 50μ 32%. The average crystal size is 71μ, (sedimentation measurements).

1) Nos. 8 and 4 = pans; No. 1 = collector.
2) In the second column of the table, Roman figures = days, arabic = hours.

Good quality bicarbonate has an apparent volume of 35, and excellent quality, consisting almost entirely of "barrels", has one of 32-33. We did not observe such values in industrial products.

Basic principles of the regulation of the crystallization process in carbonation towers. Both in the construction and the running of the tower everything is subordinated to the problem of obtaining crystals of the specified shape and size. The process of crystallization ought to proceed, as the liquid descends the tower, at a strictly controlled rate, which should differ in different zones of the tower. If this rule is broken, there are a number of serious consequences: "choking" of the column, crystallizing of the tower, obtaining bicarbonate which filters badly (high moisture content and high NaCl after filtration), lowering the output of the drying ovens, lowering the concentration of the gas from the drying ovens as a result of "cementing" the drier.

The problem of accelerating the absorption of CO_2 was solved during the development of the ammonia-soda process by the introduction of "possets" - intermediate floors with openings and bell-shaped covers over the openings. In practice the absorbing surface throughout the whole height of a tower is intentionally excessive. The problem of accelerating the absorption does not present itself to the operator of a tower: if anything has to be decided for the individual zones (bottom) of the column, it is in connection with limitation of the absorption, imposed by the requirements of the crystallization process.

In order that the dynamics of the crystallization process shall correspond to the optimum conditions for the growth and clustering of crystals, the absorption of carbon dioxide does not need to be accelerated, but to be retarded. This retardation is realized automatically by extremely ingenious means. In the initial stages of the crystallization, as already mentioned, retardation is achieved by raising the temperature of the liquid as a result of the liberation of the heat of solution of carbon dioxide and of its neutralization by ammonia together with the lower partial pressure of the CO_2 in the upper part of the column (countercurrent flow).

As the liquid flows down to the lower parts of the column, it meets gas having the highest partial pressure of CO_2. At some time - in the hot zone - the equilibrium of the reaction is slowly displaced with increase in the partial pressure of the carbon dioxide, with the result that the absorption of CO_2 becomes lower. The uniform precipitation of bicarbonate in the hot zone ensures the rapid growth of crystals, this growth occurring at the expense of the fine crystals formed in the first stages of the crystallization.

After the precipitation of the first 30 n.d. of bicarbonate the absorption at 60° and at a given concentration of gas slows down considerably. The equilibrium must be displaced by cooling the liquid. Cooling has a more potent action than changing the partial pressure of the gas. This cooling must be conducted as slowly and smoothly as possible. This runs into difficulties. At the start of the cold zone the liquid cools in each pan by 6-8°. Altogether the liquid has to be cooled by 30° in 7 pans, thus 4.5° in each pan. Actually in the lower pans only 2-3° is lost per pan, though at that point stronger cooling is permissible, because the displacement of the equilibrium at the end of the process is small. As a result of the strong cooling in the upper part of the cold zone the absorption of CO_2 increases considerably [1], which leads to the appearance of fines and nodules.

The temperature of the liquid leaving the column should be as low as possible preferably 22-23°, in order to secure the maximum coefficient of

utilization of the sodium. Such temperatures have been attained in the running of towers in some plants. To avoid considerable worsening of the quality of the bicarbonate produced, however, the temperature is not permitted to fall below 28-30°. Agitating the liquid in our towers has been shown to have a strongly negative effect, causing the cold liquid to fall to the lower part of the tower from above, and the warm liquid carrying the fines to reach the bottom more quickly than is necessary. This may be prevented or weakened by inserting intermediate floors (possets) with some openings of smaller diameter.

SUMMARY

1. Sufficiently coarse crystals of bicarbonate may be obtained even in the first stages of crystallization at any temperature, if the rate of carbonation does not exceed a definite value. It is necessary for the crystallization to start before attaining the critical point (110% carbonation). At this point a quantity of bicarbonate crystals should separate sufficient to prevent the formation of new centers of crystallization when the point at which carbamate is converted rapidly to carbonate is reached. It has been shown that in this case the sum of the saturations increases from the beginning of the crystallization up to the critical point at the expense of the "reaction supersaturation", retarding the conversion of carbamate to carbonate.

2. For each succeeding crystallization stage there also exists a definite limiting rate of carbonation, which if exceeded involves the formation of new seed crystals.

A method has been worked out for determining the limiting rate of crystallization and likewise of the average linear rate of growth of bicarbonate crystals, based on the introduction of different quantities of support crystals into the solution. By this means the minimum duration of crystallization for separate temperature zones of a tower, and of the process of carbonation as a whole, have been determined. The latter comes out at 70 minutes.

3. Bicarbonate comes down in the form of polycrystals, formed as a result of the continuous clustering together and subsequent growth of crystals. One final crystal is formed from hundreds and thousands of initial crystals.

The mechanism of clustering of the crystals – the formation of junctions between them – has been examined, and the factors have been delineated which are responsible for the form, the dimensions and limiting size of the polycrystals. A detailed analysis of the course of crystallization down a tower is given.

4. The regulation of the course of crystallization in a tower is achieved automatically by limiting the rate of absorption of CO_2 to a definite value, different for different zones of the tower. Retardation of the absorption is attained by approximating the conditions of reaction in the tower to equilibrium, at which absorption ceases.

The equilibrium in the tower is continuously and gradually displaced as a result of the raising of the partial pressure of the CO_2 and the lowering of the temperature of the liquid during its percolation down the tower. Parallel with the displacement of equilibrium the process of absorption of CO_2 is displaced and, consequently, the process of formation of bicarbonate is displaced as well.

The rate of change of the pressure of gas and of the temperature is set by the design of the column (its height and the location of the cold pans) and is also connected with the concentration of CO_2 in the gas on entry into the

tower. Unsatisfactory working of some types of tower is explained by interference with the normal gradual cooling as a result of structural defects and to non-correspondance between the actual and design concentration of gas passing through the tower.

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LIMITS OF PORTLAND CEMENT ON TERNARY DIAGRAMS

A. I. Minas

Institute of Refractories and Structural Materials of the Academy of Science of the Kazakh Federal Republic

Ternary diagrams are frequently used for visual representation of silicate systems. However, in the examination of such diagrams presented by different authors, and which contain fields corresponding to the composition of Portland cement, our attention has been drawn to divergencies between these varied representations, divergencies which are in some cases quite considerable. The aim of our paper is to delineate more precisely the field of Portland cement on ternary diagrams.

According to the classification proposed by Okorokov [1], Portland cement may be divided up in the two following ways:-

1. Depending on the ratio between the minerals and silicates:

a) alite with $C_3S:C_2S = 85:15$; b) usual composition with $C_3S:C_2S$ = from 50:50 to 85:15; c) belite with $C_3S:C_2S = 50:50$.[1]

2. Depending on the relation between minerals and matrix:

d) aluminate with $C_3A:C_4AF > 70:30$; e) usual composition with $C_3A:C_4AF$ = from 70:30 to 30:70; f) braunmillerite with $C_3A:C_4AF < 30:70$; g) ferrite with $C_4AF:C_2F < 70:30$.

Cements simultaneously belonging to two varieties can be given two classifications, e.g.: felite-braunmillerite, aluminate-alite, etc.

Since to characterize the chemical composition of Portland cement the Kind coefficient of saturation (KS) is frequently used and also the silicate (n) and aluminous (P) moduli we find it expedient to determine the limits of the separate forms of cements indicated above starting from the values KS, n, P.

As is known according to Kind the quantity C_3S in cement clinker is equal to $3.8\ SiO_2\ (1-KS)$ [3]. Hence equating the ratios

$$\frac{C_3S}{C_2S} = \frac{3.8\ SiO_2(3KS-2)}{8.61\ SiO_2(1-KS)} \quad \text{to} \quad \frac{85}{15} \text{ and } \frac{50}{50}$$

and finding KS from the equalities obtained, we determine further that to the alite cement class belong cements with $KS > 0.93$, to the belite class those with $KS < 0.81$ and those with $0.81 < KS < 0.93$ may be said to be of the usual composition.

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1) Here and elsewhere we have used the following abbreviated designations: $C_3S - 3CaO \cdot SiO_2$; $C_2S - 2CaO \cdot SiO_2$; $C_3A - 3CaO \cdot Al_2O_3$; $C_4AF - 4CaO \cdot Fe_2O_3$ and $C_2F - 2CaO \cdot Fe_2O_3$.

With $\underline{P} > 0.64$ in a cement the clinker contains, as is known, minerals-matrix: C_3A and C_4AF, and with $\underline{P} < 0.64$, C_4AF and C_2F. The quantity of C_3A in the clinker is equal to 2.65 $(Al_2O_3 - 0.64Fe_2O_3)$, the quantity of C_4AF = 3.04 Fe_2O_3 (with $\underline{P} > 0.64$) and 4.768 Al_2O_3 (with $\underline{P} < 0.64$), the quantity of C_2F is equal to 1.702 $(Fe_2O_3 - 1.567Al_2O_3)$.

Setting up the equalities: $\frac{C_3A}{C_4AF} = \frac{70}{30}$ and $\frac{C_3A}{C_4AF} = \frac{30}{70}$ (with $\underline{P} > 0.64$) and likewise $\frac{C_4AF}{C_2F} = \frac{70}{30}$ (with $\underline{P} < 0.64$), introducing the above values for C_3A, C_4AF and C_2F, replacing Al_2O_3 by $P \cdot Fe_2O_3$ and solving the equation obtained for $\underline{P}$, we find that $\frac{C_3A}{C_4AF} = \frac{70}{30}$ occurs when $\underline{P} = 3.31$ and $\frac{C_3A}{C_4AF} = \frac{30}{70}$ occurs when $\underline{P} = 1.31$; and $\frac{C_4AF}{C_2F} = \frac{70}{30}$ occurs when $\underline{P} = 0.36$.

From what has been said it can be concluded that aluminate cements have $\underline{P} > 3.31$ (approx. 3.3), usual Portland cements cover the range $1.13 < \underline{P} < 3.31$ (approx. $1.1 < \underline{P} < 3.3$), and braunmillerites the range $0.36 < \underline{P} < 1.13$ ($0.4 < \underline{P} < 1.1$) while ferrites have $\underline{P} < 0.36$ (approx. 0.4). For determination of the limits of Portland cement on ternary diagrams we must mark limits for KS, n, and P. The lower limit for KS attained in industrial cement is, as is known, 0.82 while the upper limit is 0.98 (in high quality Portland cement). The silicate modulus of Portland cement is taken, for a number of reasons, to lie within the limits of 1.9 to 5.0 (high silica Portland cement), the alumina modulus from 0.2 (ferrite cement) to 4.0.

For calculating the chemical composition of cement corresponding to different values of KS, n, and P we use an expression actually with $\underline{P} \geq 0.64$: quantity

$$Fe_2O_3 = \frac{100}{(P + 1)[n(2.8KS + 1) + 2.65] - 1.3} \quad [2]$$

For cases with $\underline{P} < 0.64$, analogous expressions are derived from the known Kind equality connecting the moduli:

$$Fe_2O_3 = \frac{\Sigma}{(m + 1)(n + 1)(P + 1)},$$

where Σ = sum of the main oxides and m = hydraulic modulus. Taking for the construction of ternary diagrams $\Sigma = 100\%$, expressing n by the main oxides and CaO by KS, and the acid oxides (by means of an expression for KS which in the given case has the following form):

$$KS = \frac{CaO - 1.1Al_2O_3 - 0.7Fe_2O_3}{2.8SiO_2}$$

and by further substituting $Al_2O_3 = PFe_2O_3$ and $SiO_2 = n(P + 1) \cdot Fe_2O_3$ (obtained from the expression for the alumina and silicate moduli) after rearrangement we get

$$Fe_2O_3 = \frac{100}{(P + 1)[n(2.8KS + 1) + 2.1] - 0.4}$$

Calculations of the composition of Portland cement (for $\Sigma = 100\%$) are given in Table 1. For these calculations the following values of KS were taken: 0.82, 0.93 and 0.98; for n, 1.9 and 5.0 (intermediate values of n were not necessary for the construction of fields on the diagrams); for P 0.2, 0.36, 1.13, 3.31 and 4.0.

From Table 1 it can be seen that the weight of CaO in Portland cement clinker can vary from 63.84 to 71.66% of the sum of the main oxides, SiO_2 from 19.95 to 27.40% Al_2O_3 from 0.81 to 9.24%, and Fe_2O_3 from 0.95 to 10.38%.

The limits of content of the main oxides in different forms of Portland cement are given in Table 2 (compiled on the basis of Table 1).

On the basis of Table 1 the Portland cement fields have been delineated on the diagrams; $CaO-SiO_2-R_2O_3$, $CaO-SiO_2-Al_2O_3$ and $SiO_2-Al_2O_3-Fe_2O_3$.

Diagram $CaO-SiO_2-R_2O_3$. The field of Portland cement on this diagram is shown in Figure 1a. In Figure 1b part of this diagram is given on a larger scale: the point A corresponds to Portland cement having KS = 0.82, n = 5.0 and P = 0.2; the point C to a Portland cement with KS = 0.82, n = 1.9 and P = 0.2; the point D to a cement with KS = 0.98, n = 1.9, P = 4.0; and the point F to a cement with KS = 0.98, n = 5.0 and P = 4.0. The field is bounded by the straight lines: AB, for cements with KS = 0.82, P = 0.2, n = 1.9-5.0
CD, for cements with KS = 0.82-0.98, n = 1.9, P = 0.2-4.0
DE, for cements with KS = 0.98, n = 1.9-5.0, P = 4.0
AE, for cements with KS = 0.82-0.98, n = 5.0, P = 0.2-4.0

It should be noted that for each value of n there is a corresponding straight line on the field. Thus on the line BE are located cements with n = 3. The general points of interesection obtained by extending the lines corresponding to different values of n is the lower left angle of the ternary diagram (Figure 1).

Each point in the general field ABDE corresponds to a number of cements having different values of KS and P but the same value of n.

Diagram $CaO-SiO_2-Al_2O_3$. In Figure 2a is shown the field of Portland cement in this diagram.

The same field is shown enlarged in Figure 2b. Point A represents a cement with KS = 0.82, n = 5.0, P = 0.2, Point B a cement with KS = 0.82, n = 1.9, P = 4.0 and point C a cement with KS = 0.98, n = 1.9, P = 4.0; point D a cement with KS = 0.98, n = 1.9 and P = 0.2.

The line AB comprises cement with KS = 0.82; the line CD cements with KS = 0.98, n = 1.9 and P = 0.2-4.0, the line AD cements with P = 0.2 and the line BC cements with n = 1.9 and P = 4.0.

Diagram $SiO_2-Al_2O_3-Fe_2O_3$. We know of no instances of the use of these diagrams for showing fields occupied by Portland cement; however, in the given case, they are of some interest. In Figure 3a is given the diagram for $SiO_2-Al_2O_3-Fe_2O_3$.

The base of the diagram correponds to the materials having n = 0, and the apex to those having n = ∞. The left boundary of the diagram (with Fe_2O_3 = 0) corresponds to material with P = ∞ and the right (with Al_2O_3 = 0) to those having P = 0. The field of Portland cement is shown on a larger scale in Figure 3. Since CaO is absent from this diagram, the position of points corresponding to individual cements does not depend on KS but only on n and P. The lines corresponding to different silicate moduli of cements is parallel to the base of the diagram. The line JF corresponds to n = 1.9; MN to n = 3; RP to n = 4; AE to n = 5. The point of intersection of lines corresponding to different aluminate moduli is the apex of the diagram. The line EF corresponds to P = 0.2; DG to P = 0.36; CH to P = 1.13; BT to P = 3.31 and AJ to P = 4.

Hence the rectangle DEFG is the field of ferritic cements, CDGH braunmillerite,

TABLE 1

Composition of Portland cements

KH	n	P	Content (in %) (for Σ = 100%)				Al_2O_3 + Fe_2O_3 (R_2O_3)	Content (in %) (for CaO + SiO_2 + Al_2O_3 = 100%)		
			CaO	SiO_2	Al_2O_3	Fe_2O_3		CaO	SiO_2	Al_2SO_3
0.82	1.9	0.2	63.84	23.70	2.08	10.38	12.46	71.24	26.44	2.32
	1.9	0.36	64.05	23.55	3.28	9.12	12.40	70.46	25.92	3.62
	1.9	1.13	65.05	22.90	6.39	5.66	12.05	68.96	24.26	6.78
	1.9	3.31	66.27	22.10	8.93	2.70	11.63	68.16	22.68	9.16
	1.9	4.0	66.52	21.93	9.24	2.31	11.55	68.13	22.41	9.46
	5.0	0.2	67.12	27.40	0.91	4.57	5.48	70.32	28.73	0.95
	5.0	0.36	67.18	27.35	1.45	4.02	5.47	70.01	28.48	1.51
	5.0	1.13	67.56	27.03	2.87	2.54	5.41	69.37	27.69	2.94
	5.0	3.31	68.14	26.55	4.08	1.23	5.31	69.00	26.86	4.14
	5.0	4.0	68.20	26.50	4.24	1.06	5.30	68.91	26.79	4.28
0.93	1.9	0.2	66.29	22.08	1.94	9.69	11.63	73.40	24.45	2.15
	1.9	0.36	66.50	21.96	3.05	8.49	11.54	72.68	23.98	3.34
	1.9	1.13	67.40	21.38	5.95	5.27	11.22	71.16	22.56	6.28
	1.9	3.31	68.42	20.70	8.35	2.53	10.88	70.18	21.25	8.57
	1.9	4.0	68.54	20.61	8.68	2.15	10.85	70.07	21.05	8.88
	5.0	0.2	69.64	25.30	0.84	4.22	5.06	72.72	26.40	0.88
	5.0	0.36	69.76	25.20	1.33	3.71	5.04	72.44	26.18	1.38
	5.0	1.13	70.12	24.90	2.64	2.34	4.94	71.84	25.46	2.70
	5.0	3.31	70.60	24.50	3.77	1.19	4.90	71.41	24.78	3.81
	5.0	4.0	70.62	24.48	3.92	0.98	4.90	71.36	24.69	3.95
0.98	1.9	0.2	67.34	21.40	1.88	9.38	11.26	74.31	23.61	2.08
	1.9	0.36	67.49	21.30	2.96	8.25	11.21	73.55	23.11	3.23
	1.9	1.13	68.37	20.73	5.78	5.12	10.90	72.08	21.82	6.10
	1.9	3.31	69.36	20.07	8.11	2.45	10.56	71.10	20.58	8.32
	1.9	4.0	69.55	19.95	8.40	2.10	10.50	71.05	20.37	8.58
	5.0	0.2	70.72	24.40	0.81	4.07	4.88	73.72	25.43	0.85
	5.0	0.36	70.78	24.35	1.29	3.58	4.87	73.41	25.25	1.34
	5.0	1.13	71.02	24.15	2.56	2.27	4.83	72.67	24.72	2.61
	5.0	3.31	71.50	23.75	3.65	1.10	4.75	72.28	24.08	3.69
	5.0	4.0	71.56	23.70	3.79	0.95	4.74	72.24	23.93	3.83

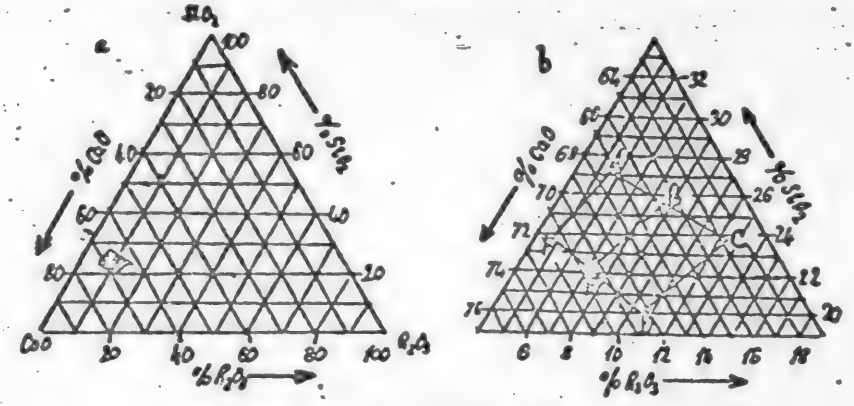

Fig.1. Diagram of $CaO-SiO_2-R_2O_3$.
a) Field of Portland cement on diagram b) Portion of diagram on larger scale (explanation of symbols given in the text).

TABLE 2

Content of main oxides in different forms of Portland cement

Basic classification	Name of cement	Content (in %) (for $CaO + SiO_2 + Al_2O_3 + Fe_2O_3$ = 100%)			
		CaO	SiO_2	Al_2O_3	Fe_2O_3
Mineral silicates	Usual composition (KS=0.82:0.93)	63.84-70.62	20.61-27.40	0.84-9.24	0.98-10.38
	Alite (KS=0.93:0.98)	66.29-71.56	19.95-25.30	0.81-8.68	0.95-9.69
Minerals-matrix	Aluminate (P=3.31:4.00)	66.27-71.56	19.95-26.55	3.65-9.24	0.95-2.70
	Usual composition (P=1.13:3.31)	65.05-71.50	20.07-27.03	2.56-8.93	1.10-5.66
	Braunmillerite (P=0.36:1.13)	64.05-71.02	20.73-27.35	1.29-6.39	2.27-9.12
	Ferrite (P=0.2:0.36	63.84-70.78	21.30-27.40	0.81-3.28	3.58-10.38

BCHI of ordinary, and ABIJ of aluminate, Portland cements.

Each point of the field corresponds to a cement with one value of n and one value of P.

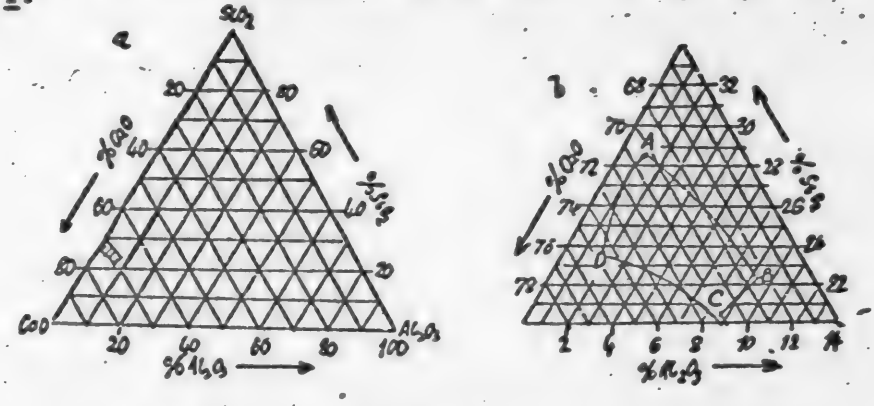

Fig.2. Diagram $CaO-SiO_2-Al_2O_3$.
a) Field of Portland cement on diagram; b) Portion of diagram enlarged (explanation of symbols given in test).

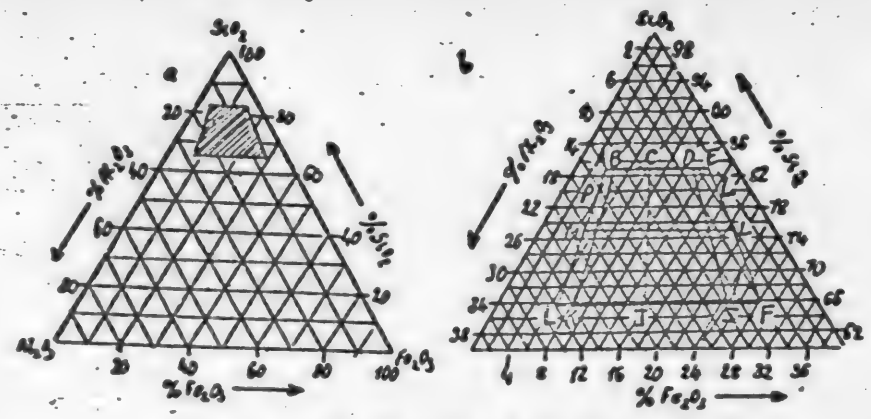

Fig.3. Diagram SiO_2-Al_2O_3-Fe_2O_3.
a) Field of Portland cement on diagram; b) Portion of diagram enlarged (explanation of symbols given in text).

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POROSITY OF ELECTRO DEPOSITED NICKEL

A.A.Sutyagina and A.P.Vagramyan

Elucidation of the cause of pores formation in deposits is one of the more important problems related to the electrolytic deposition of metals. Usually the term "pores" includes macro- and microcanals, leading from the surface of the deposits to the foundation metal of the cathodes. In electrolytically - obtained metal deposits the pores have varying dimensions, so that it is very difficult to determine exactly their number and size. Depending on the conditions and duration of the experiment, for one and the same coating, pores may or may not be discovered. Thus, in experiments in liquids with samples covered with a protective layer of definite thickness, the deposits may be non-porous, while in an atmosphere of corrosive gases pores may be observed. Thus, the evaluation of the porosity of the deposits is relative.

Pores may be divided into two groups, on the basis of their size: 1) coarse pores, formed mainly as a result of non-homogeneity of the electrode surface, which may be conditioned by different kinds of inclusion - non-metallic, foreign metals, oxides, surface-active substances, etc.; 2) fine pores, determined by the structure of the deposits (form dimensions, and arrangement of crystals), depending on the conditions of electrolysis.

The difficulty of investigating the porosity of electrolytic deposits lies basically in the absence of an accurate quantitative method of examining pores. The use of such a quantitative method and the study of porosity is complicated by the fact that pores themselves have different forms and sizes.

Relatively little work has been devoted to the study of porosity, and the greater part of it has been concerned with the study of separate questions of the electrodeposition of metals.

In this paper the study of the effect of various factors on the porosity of electrolytic deposits of nickel is reported.

EXPERIMENTAL

The electrodeposition of nickel was carried out in the main in a bath having the following composition (in g/liter): $NiSO_4 \cdot 7H_2O$ – 166; H_3BO_3 – 30; $Na_2SO_4 \cdot 10H_2O$ – – 50; $MgSO_4 \cdot 7H_2O$ – 20 and NaCl – 2.

The electrolysis was carried out in closed glass vessels. The volume of electrolyte was 0.5 liter. Chemically pure nickel was used as an anode, and iron plates of 2 cm^2 surface area were used as cathodes. The temperature was 17-20°.

Method of examining the pores. To examine the pores in the electrolytic deposits of nickel on iron samples, we usually used a potassium ferricyanide reagent of the following composition (in g/liter) $K_3Fe(CN)_6$ – 10 and NaCl – 20.

The serviceability of the method is due to the fact that the reagent, penetrating through the pores of the covering to the base metal, reacts with it, and the product of reaction (Turnbull's blue) comes out through the pores to the surface, forming a blue patch. The number of pores is taken as being equal to the number of blue patches.

In this work the porosity was determined as follows.

The sample under investigation was dipped into a solution of the reagent of the indicated composition for two minutes, after which it was washed with distilled water and dried with filter paper. The number of pores was counted under a microscope having a magnification of 50. To facilitate counting the total number of pores, the surface of the sample was divided into separate squares, making it possible to count the pores accurately. Counting the pores under the microscope makes it possible to distinguish a large number of fine pores which could not be distinguished with the naked eye.

Effect of support and of previous treatment on the porosity. The preliminary preparation of the cathode surface had a considerable influence on the porosity of the electrolytic deposits [1-3]. We studied the effect of different kinds of treatment of the cathode on the porosity of electrolytic deposits of nickel. Deposits obtained on cathodes previously rubbed down with emery paper of different number had different numbers of pores, and the rougher the treatment of the surface of the electrode, the larger the number of pores formed in the deposit; the smoother the surface of the cathode, the lower the number of pores in the deposit.

After mechanical treatment with emery paper No.120 the samples were subjected to various chemical treatments: de-greasing with 10% NaOH, electro-chemical de-greasing with 10% NaOH, de-greasing with 20% Na_2CO_3 at a temperature of 80°, and mechanical rubbing of moist samples with soda and subsequent treatment in acid solutions.

The best results were obtained after rubbing the damp samples with soda. Apparently in this case the various foreign particles adhering to the surface as a result of mechanical treatment are more effectively removed, and consequently the number of pores diminishes sharply.

On the basis of experiments on the effect of previous treatment on the number of pores in the electrolytic deposits, "standard" conditions of preparation of the cathode were selected, as follows: the samples were rubbed down with emery paper No.120, washed with water, de-greased by rubbing with soda to complete wetting, and washed with distilled water. After being prepared in this manner, the samples were used for the deposition of nickel on them. As indicated above, if the covering of metal is not homogeneous, i.e., if it has various inclusions, the number of pores in the deposit increases sharply. Thus, for example, non-metallic inclusions obtained in the surface of the cathode as a result of its mechanical treatment, foreign metals (impurities), traces of grease and of surface active substances remaining as a result of poor de-greasing of the electrode, scale. etc., induce the formation of porous deposits.

Metallic inclusions which lower the hydrogen overvoltage have a particularly strong influence on the porosity. During the process of electrolysis, the parts of the cathode which lower the hydrogen overvoltage are, at the same time, the very parts which have a high overvoltage for the separation of metal [4], hence on these parts an intense liberation of hydrogen occurs, while the separation of metal on them is considerably lowered. The intensive separation of hydrogen at these parts of the cathode leads to the formation of crater-like hollows, in the centre of which there are canals reaching to the base metal.

The continuous separation of hydrogen leaves behind a perceptible trace in the form of striae on the surface of the cathode.

If the sample is sectioned at the place where such craters are formed, and if polished microscope samples are then prepared from the pieces, it can be seen that coarse pores in the deposit are actually formed directly at the site of the inclusion. Along with the coarse pores many fine ones are formed.

It should be noted that pores may be formed not only on the parts whose hydrogen overvoltage is reduced, but also on parts not properly de-greased and therefore poorly wetted by the electrolyte.

In a series of papers [5] it has been shown that the degree of adherence and the dimensions of the bubbles of hydrogen at the moment of liberation depend on the ratio of surface tensions at the boundaries solution/gas, solution/metal and metal/gas, i.e., on the contact angle. The contact angle changes considerably in the presence of surface-active substances in the electrolyte.

In the absence of contamination the magnitude of the contact angle depends on the electrode potential. As the polarization curve changes, the dependence of the contact angle (ϑ) on the potential (φ) of the electrode passes through a maximum [6].

Thus, the duration of adherence of the bubbles can be changed both by changing the concentration of surface-active substances, and by changing the current density at the cathode. On the parts of the cathode where bubbles of hydrogen adhere, the separation of metal is hindered for a considerable time [7], as a result of which pores are formed.

Effect of thickness of coating on the porosity. It is evident that, with identical quantities of metal deposited, the degree of filling up of the surface of the electrode by crystals will vary, depending on the size of the crystals. If the crystals are coarse, only a small part of the surface of the electrode will be covered by the deposit, while the same quantity of metal deposited in the form of fine crystals will cover the entire surface with a uniform deposit.

To fill up all the defects of the cathode surface with deposited metal (coarse crystals) in order to obtain a non-porous deposit, it is necessary to separate from the electrolyte a considerably larger quantity of metal than when depositing fine crystals on the surface. Thus, for every given dimension of crystal, there should be a minimum quantity of metal which will cover the whole surface. Such a quantity of metal may be called the "critical" one. Since the average thickness of the deposit is proportional to the quantity of metal deposited on the cathode, it can be said that the critical thickness necessary to ensure absence of pores will differ with the size of the crystals.

Consequently, as the size of the crystals increases the minimum thickness necessary to obtain a non-porous deposit should be larger.

If the curve of dependence of the number of pores on the thickness of the covering is plotted for different crystal sizes, these curves being for crystals oriented and lying compactly on one another, then there should be a sharp bend in it corresponding to complete covering of the given surface with crystals and the formation of a non-porous covering.

In order to obtain a non-porous deposit with a small thickness of covering, it is necessary to select the condition of electrolysis at which uniform, finely-crystallized, dense deposits are obtained.

Under the practical conditions of electrolysis, the crystals are arranged largely at random, without any special orientation, and it is natural that the relation between the size of the crystal and the minimum thickness should be more complex, and the bend of the curve "number of pores against thickness of deposit" should be rounded. In cases of random crystal distribution, the minimum thickness necessary to ensure a non-porous covering will be considerably larger than the thickness starting from crystals compactly disposed relative to one another.

In Fig. 1 are presented the results of the investigations of the dependence of the porosity on the thickness of nickel coating (5-55μ). Nickel was deposited electrolytically on iron electrodes given the "standard" pre-treatment. The electrolyte was of the composition indicated above, the current density 2A/dm^2, and the temperature 17-20°. To plot the curves of dependence of porosity on the thickness of covering, an average thickness of covering was selected which was determined from the general increase of weight relative to the whole surface of the electrode. From Fig. 2. it is evident that as the thickness increases, the number of pores falls sharply up to a thickness of the order of 15-17μ, after which the curve changes direction and, as the thickness increases further, the number of pores changes comparatively slowly.[1] Completely non-porous deposits were not obtained even when the thickness was increased to 55μ. In the portions I-II the large number of pores was due to the fact that the thickness of the deposit was not "critical", but in the portion II-III the presence of pores in the deposit was caused by the non-homogeneity of the surface of the foundation metal of the cathode.

Effect of current density on the porosity of electrodeposited nickel. In Fig. 2 are shown curves of the relation between the number of pores formed in the nickel covering and the current density. The deposits were obtained on iron electrodes, treated in the "standard" manner, the thickness of the covering being 17-20μ.[2] As can be seen from this figure the number of pores passes through a minimum at a certain current density. The smallest number of pores in the deposit, at the given composition and temperature, is obtained at a current density of 2 A/dm^2. The fact that the number of pores in the deposit, when plotted against current density passes through a minimum may be explained as follows.

A dense and uniform metallic deposit is obtained over a definite interval of current density. The large number of pores obtained in the electrolytic deposition of nickel at lower current densitites may be due to the following causes:

1) if the rate of deposition of nickel crystals is less than the rate of passivation, the growing crystals will rapidly become passivated, their growth will be interrupted [8], the connection between separate crystals will become more tenuous and the deposit will be loose and porous;

2) at low current densities the deposition of metal occurs mainly on the more active parts of the surface because of the comparatively small polarization of the cathode.

As a result of this the deposition of metal is not uniform over the entire surface, but occurs on separate parts of the surface of the cathode.

As the current density increases, the metal deposits on the less active parts [9], and, at some values of the c.d. the deposits obtained are more compact and uniform, as a result of which the number of pores is reduced to a minimum.

With further elevation of the current density the number of pores increases, as a result of the intensive discharge of hydrogen, which is controlled by the current efficiency for nickel (Fig. 3).

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[1]) In studying the dependence of the number of pores on samples of different kinds of iron, the absolute number of pores changed somewhat, but the dependence remained the same.

[2]) Change of thickness from 17-20μ scarcely affected the number of pores, as can be seen from Fig. 1.

Effect of surface-active substances on the porosity of electro-deposited nickel. The effect of various surface-active substances (acetone, formaldehyde, n-cresol, 2,6-and 2,7-naphthalenedisulfonic acids, etc.) on the porosity of nickel deposits was studied.

The results of the investigation of the dependence of the number of pores on the current density with different additives is given in Fig. 4.

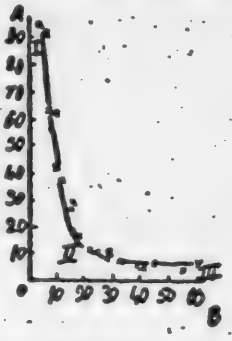

Fig. 1. Dependence of the number of pores on the thickness of nickel covering. A = Number of pores; B = thickness of covering (in μ).

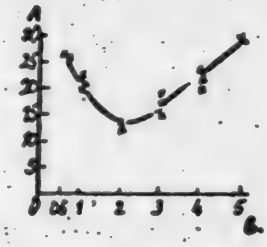

Fig. 2. Dependence of the number of pores formed in the nickel covering on the current density at the cathode. A = Number of pores; B = current density (in A/dm^2).

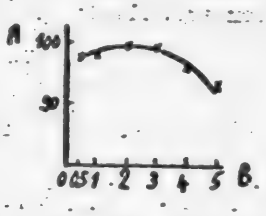

Fig. 3. Current efficiency for the deposition of nickel from solution without additives as a function of current density. A = Current efficiency (in %); B = current density (in A/dm^2).

As can be seen from Fig. 4, in the presence of organic surface-active substances, the number of pores as a function of current density passes through a minimum, and this minimum, for additives such as acetone, formaldehyde, 2,6- and 2,7-naphthalenedisulfonic acids, is displaced towards lower current densities in comparison with the minimum of the porosity curve for a pure electrolyte.

From Fig. 4 it is evident that the minimum number of pores in the deposit during electrodeposition of nickel was formed from a solution to which the

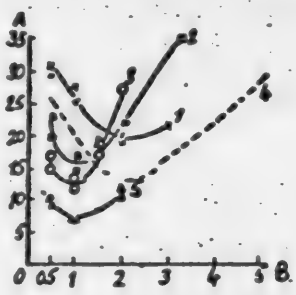

Fig. 4. Dependence of the number of pores formed in a nickel deposit on the current density at the cathode with various surface-active substances as additives.

A = Number of pores; B = c.d. (in A/dm^2), The following were added to the electrolyte: 1 - 0.15 g cresol/liter; 2 - formaldehyde 8 ml/liter; 3 - acetone 8 ml/liter; 4 - no additive; 5 - 2,6- and 2,7-naphthalenedisulfonic acids, 3 g/liter (composition of the electrolyte in these experiments in g/liter: $NiSO_4 \cdot 7H_2O$ - 210; H_3BO_3 - 30; NaCl - - 3; NaF - 6. The composition given was that proposed by Kudryavtsev [10]).

2,6- and 2,7-naphthalenedisulfonic acids, proposed by Kudryavtsev had been added.

The displacement of the minimum of the curve for pure electrolyte when surface-active substances are introduced is due to the fact that after the introduction of such additives, compact and uniform deposits are obtained only at lower current densities. It has been shown by Loshkarev and co-workers that when surface-active substances are introduced into the electrolyte the current density necessary for the production of compact and uniform deposits is lowered.

Thus, the displacement of the minimum of these curves towards lower current densities is conditioned by the fact that more compact and uniform deposits are obtained only at low current densities.

Increase of the number of pores with increase of current density in the presence of certain substances (formaldehyde, acetone) is caused by the fact that these substances are extensively reduced on separate parts of the cathode surface, causing pores to be formed similar to those when hydrogen separates on the cathode.

SUMMARY

1. It has been established that the number of pores of electrodeposited nickel decreases sharply with increasing thickness up to a definite limit: with further increase of the thickness, the number of pores change very little.

2. It has been shown that the plot of the number of pores against the current density passes through a minimum.

3. It has been established that when surface-active substances are added, the number of pores may be decreased or increased by comparison with the number formed in an electrolyte without such additives.

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ELECTRODEPOSITION OF COBALT

P.N.Kovalenko

V.M.Molotov State University, Rostov - on - Don

Existing methods for the electrolytic determination of cobalt and for its separation from other metals suffers from a number of deficiencies, due to the tendency of cobalt to oxidize and to deposit on the anode in the form of an oxide [1]. The usual method for the electrolytic deposition of cobalt from ammoniacal solution requires strict control of the cathode potential; under adverse conditions the metal is deposited on the cathode in a spongy form and on the anode as a peroxide. It has been recommended to determine the small quantity of cobalt remaining in the solution colorimetrically [2]. Lundel and Gofman added sodium sulfite to the ammoniacal solution for the electrodeposition of cobalt [3]. However, in this case the deposits of metallic cobalt always contain elementary sulfur [2]. Some investigators have used oxalates as buffers, but obtained unsatisfactory results because the metal separating at the cathode always contained carbon [2, 4].

As was shown in the experimental part of our work, oxalates are excellent additions for the electrodeposition of cobalt; when a definite concentration of hydrogen ions is present, and within known temperature limits, a lustrous deposit of cobalt is obtained, adhering firmly to the cathode and containing no carbon.

EXPERIMENTAL

In order to study the problem of avoiding the separation of cobalt as oxide at the anode and as a spongy metallic deposit at the cathode, we studied the effect of a number of factors on the behavior of cobalt during electrolysis: the concentration of ammonium oxalate, the pH, and the temperature of the solution. The pH was determined by the Boggendorff compensation method, using a hydrogen electrode. The temperature was maintained within $\pm$ 0.5°, by a water thermostat. Gauze electrodes were used (Fischer). The investigation was carried out at pH's of 2, 4, 6, 8 and 10, at temperatures of 20, 40, 60,80 and 100° and at concentrations of ammonium oxalate of 0.21 and 0.28 mol/liter. The concentration of cobalt sulfate was 0.06 N.

Effect of pH of the buffered oxalate solution on the decomposition potential and the discharge potential of cobalt. In the electrolysis of cobalt from a solution containing 0.21 mol/liter of ammonium oxalate, of pH 2, a perceptible decomposition of the oxalate was observed. The rate of electrodeposition of cobalt was not very fast; in two hours of electrolysis, 8% of it separated in the form of a friable, grainy deposit. When the pH was raised to 4, the rate of deposition of metal was considerably increased; in the course of two hours 57.3% of the cobalt separated out. The decomposition potential increased considerably at the same time (1.12 to 1.7 V). The discharge potential remained considerably more negative. The quality of the deposit had improved considerably; it was dense, fine grained, but already dull gray, with a blackish tinge. Raising the pH of the solution to 6 increased the rate of electrolysis still more; in the course of 2 hours the cobalt was completely discharged, but the qualtity of the deposit

was even worse than in the electrolysis of metal at pH 2. From being gray, as in the preceding cases, the deposit of cobalt became blackish-brown as a result of precipitation of carbon formed by reduction of the oxalate ions. Adjusting the pH to 8 caused the rate of electrolysis to be lowered by a factor of approximately 5 (22.5%); the quality of the precipitate improved however, but the deposit was not distributed uniformly over the surface of the electrode. Finally, by increasing the pH to 10, the rate of deposition of cobalt was increased again; in two hours~ 60% of metal was discharged.

Adjusting the electrolyte to a strongly alkaline reaction with ammonia increased the amount deposited on the cathode (~ 88.2%). However, analysis of the brown deposit separated showed that it contained only 27% of metallic cobalt. The rest was impurity composed of products of the breakdown of ammonium oxalate.

According to Klassen [5], oxalate ions decompose under the influence of an electric current with formation of NH_3 and CO_2; carbon dioxide is then reduced to carbon, which precipitates along with metallic cobalt. Later investigations showed that, when using oxalates, carbon may separate either in the purely colloidal state or in the form of carbon-containing compounds, the formation of which is explained by the movement of the colloid particles to the cathode [4]. The metallic cobalt formed apparently acts catalytically, only facilitating the decomposition of the oxalate ions.

This decomposition of ammonium oxalate was fairly extensive in our experiments at almost all pH values.

The results of this series of experiments are given in Table 1, the data of which shows that the magnitude E_p grows with increase of pH. The residual increase of decomposition voltage in going from pH 4 to 6 (for 0.21 mol/liter of ammonium oxalate solution) is due to a change of the anode process which causes a sharp reduction of the anode potential for this change in value of the acidity.

The results of this series of experiments are set forth in Table 1, showing that E_r steadily increases as the pH increases. The absence of any increase in the decomposition potential between pH's of 4 and 6 is connected with a change in the anode process, which causes a sharp lowering of the anode potential between these pH values. Increase in the values of E_r and E_k as the pH increases indicates that a very much more stable oxalate complex is formed with the cobalt ion. This increase in the stability of the complex results in a resistance to its decomposition at the cathode.

The rate of deposition of cobalt is higher on the average at a pH of 6. However, the quality of the precipitate is better at a pH of 4; consequently this pH is the optimum in the given circumstances. It is important to note that the current strength at the moment of discharge of cobalt ions is raised, but the current strength at the beginning of electrolysis is lowered, by increase of pH (Fig.1). This apparently is due to a change in the mobility of the complex ions of cobalt.

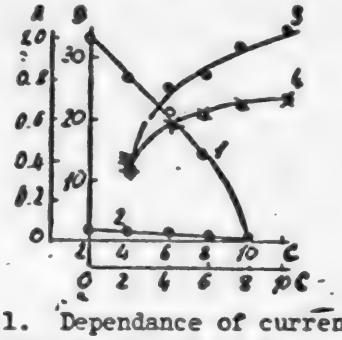

Fig.1. Dependance of current strength on the Ph of ammonium oxalate. A = Initial current strength (in mA); B = current strength when discharging Co ions; C = concentration of hydrogen ions of the buffer solution. Initial current strength: 1 = 0.21 mol/liter of solution of ammonium oxalate; 2 = 0.28 mol/liter of solution. Current strength during discharge of Co: 3 = 0.21 mol/liter ammonium oxalate and 4= = 0.28 mol/liter ammonium oxalate.

With increase of the concentration of ammonium oxalate at the same pH the rate of electrodeposition of Co was observed to diminish (Table 1). Evidently, in the given case an increase in concentration of ammonium oxalate increases the stability of the complex ion. It was earlier shown by us [6] that the concentration of the buffer solution has a great influence on the rate of electrodeposition of metal. Thus, in the study of the effects of concentration of sodium citrates and tartrates on the rate of electrodeposition of copper, bismuth, cadmium, and lead, it was discovered that as the concentration of these buffers increased, the quantity of metal deposited decreased, apparently as a result of a diminution of the mobility of complex ions.

TABLE 1

Effect of pH of Oxalate Solutions on the Decomposition Voltage and the Discharge Potential of Co

pH	Concentration of ammonium oxalate (in mol/liter)	Decomposition voltage, E_p for Co (V)	Discharge potential E_p, for Co (V)	Quantity of metal deposited in 3 hours of electrolysis (g)	Quantity of metal deposited in 3 hours of electrolysis (%)	Voltage at which Co deposits (V)	Quality of deposits
2	0.21	1.12	-0.105	0.00142	8.0	2.0	Friable, rough
4	0.21	1.70	-0.459	0.0102	57.3	2.4	Dense, fine grained dull gray.
6	0.21	1.67	-0.596	0.0178	100.0	2.4	Blackish-brown.
8	0.21	2.05	-0.604	0.004	22.5	2.7	Dense, dull difficult to distinguish from platinum, yellow in places.
10	0.21	2.10	-0.627	0.0106	60.0	2.7	Yellowish, dull not uniformly distributed
Strongly ammoniacal	0.21	2.20	-0.798	0.0165	88.23	2.5	Blackish and friable
2	0.28	1.15	-0.197	0.00	0.00	1.80	-
4	0.28	1.25	-0.390	0.0066	37.8	1.80	Yellowish gray, uniform
6	0.28	1.47	-0.485	0.0120	67.4	1.80	Gray, adhering well
8	0.28	1.56	-0.445	0.0014	7.86	2.0	Pale yellow, dull, uniform
10	0.28	2.06	-0.592	0.0136	76.1	2.7	Black, slightly rough

From Table 1 it is evident that while in the electrolysis of cobalt in 0.28 mol ammonium oxalate at pH2 the value of E_p is larger and the value of E_k is more negative than in 0.21 mol solution of the buffer, at other pH values such an elevation was not observed. It is evident that in 0.28 mol solution of ammonium oxalate at pH's of 4, 6, 8 and 10 the decomposition of oxalates, as a result of cathodic depolarization, proceeds vigorously, as is shown by the decomposition potential and the discharge potential for cobalt.

Effect of temperature on the potentials of decomposition and discharge of cobalt. In order to find the optimum temperatures for the electrolysis of solutions and to study their effect on the course of electrodeposition of cobalt, experiments were carried out at the optimum pH of 4, at ammonium oxalate concentrations of 0.21 and 0.28 mol/liter, and at temperatures of 20, 40, 60 80 and

100°. The results of these investigations are shown in Table 2.

TABLE 2

Effect of Temperature on the Decomposition Voltage and Discharge Potential for Cobalt

Temperature of solution (in °C)	Concentration of ammonium oxalate (in mol/liter)	Decomposition voltage, E_p for Co (V)	Discharge potential E_p for Co (V)	Quantity of metal deposited in 3 hours of electrolysis (g)	Quantity of metal deposited in 3 hours of electrolysis (%)	Voltage at which Co deposits (V)	Quality of deposits
20	0.21	1.70	-0.459	0.0102	57.3	2.4	Dense, fine grained, matte gray
40	0.21	1.35	-0.466	0.0122	68.53	2.0	Slightly matte hard, with black streaks
60	0.21	1.26	-0.490	0.0139	72.40	1.8	Dark gray, non-uniform, dense
80	0.21	1.20	-0.493	0.0161	90.94	1.7	ditto
100	0.21	1.15	-0.505	0.0178	100.0	1.8	Fine grained, lustrous, dense, uniform
20	0.28	1.25	-0.390	0.0066	37.8	1.8	Yellow-gray, uniform
40	0.28	1.20	-0 393	0.0016	9.0	1.9	Black, dull, dense
60	0.28	1.20	-0.466	0.0115	64.5	1.8	Matte, dark gray, non-uniform
80	0.28	1.20	-0.495	0.0176	99.0	1.8	Dark and gray matte
100	0.28	1.00	-0.520	0.0053	29.0	1.7	Dense, lustrous, fine grained.

In the electrolysis of cobalt in 0.21 mol/liter ammonium oxalate at 40° no marked separation of gas bubbles was observed on the cathode or anode but instead a brown streaky deposit appeared on the points of contact of the glass anode supports with the walls of the cathode, which was evidence of the simultaneous formation of gas and separation of metal. At 60° the deposit of cobalt was friable dark gray and not uniformly distributed on the cathode, and simultaneously there was vigorous gas formation on the electrodes. Raising the temperature to 80° improved the qualtity of the deposit; it became denser and adhered more strongly to the cathode, although it remained dark gray. The cobalt deposited more compactly on solid cathodes than on gauze ones. Only by raising the temperature to 100° was it possible to obtain cobalt in the form of a lustrous, dense, uniformly-distributed deposit. Electrolysis with complete deposition of a metal, carried out at 100° from 0.21 mol/liter ammonium oxalate at pH 4 (voltage 1.8 V) lasted in all 50-60 minutes if the potential was not increased gradually, but immediately brought up to 1.8V, at which the current strength increased to 1.2A. Under these conditions cobalt precipitated in the form of fine grained, dense, lustrous deposits adhering well to the cathode. The fact that the cobalt had deposited completely was checked by polarography and by reaction with Na_2S.

As is shown in Table 2, raising the temperature of the solution caused a linear increase in the quantity of metal precipitated, which at 100° became 100%. Here there was observed a phenomenon which was considered worthy of special note. While in all cases of electrodeposition of cobalt at buffer solution

temperatures of from 20-80° there was observed decomposition of the ammonium oxalate with formation of carbon, having a decided influence on the quality of the deposited metal, at temperatures of 95-100° the decomposition of ammonium oxalate was accompanied by the separation of CO_2 and the contamination of the cobalt deposit ceased.

Such a phenomenon was observed by Izgaryshev and Aryamova in a study of the cathodic reduction of oxalic to glyoxylic and glycolic acids in the presence of sulfuric acid, using lead and lead-amalgam cathodes. Platinum, copper, nickel, graphite and stainless steel cathodes did decompose oxalic acid; only hydrogen separated. Izgaryshev and Aryamova suggested that the different decomposition effects at different electrodes are due to the very large overvoltage on the first electrode by comparison with that on the second.

It may be suggested that the cobalt separated at the cathode catalyzes the decomposition of oxalic acid, so that with increase of temperature to 95-100°, the decomposition goes to carbon dioxide, which escapes from the solution as bubbles of gas. In our case the high quality of the deposit of metallic cobalt is due to the high temperature and, in part, to the definite value of the pH of the solution, to which no attention has been paid in electrolytic analysis, where the deposition has been carried out in oxalate-buffered solution.

Figs. 2 and 3 show the character of the fall of decomposition voltage and the displacement of the discharge potential towards negative values with increase of temperature. The lowering of the decomposition voltage with increase of temperature is due to the gradual reduction of the anode potential (Fig. 2).

As observed also in the electrolysis of cobalt in 0.28 mol/liter ammonium oxalate (pH = 4), its rate increases in the temperature interval of 40-80° and upon reacting temperature of 100° unexpectedly drops. However, at 100° the deposit of metal, as in the electrolysis of the 0.21 mol buffer solution, is of good quality (fine grained, dense and lustrous). In the given case the decomposition of ammonium oxalate to carbon was also not observed. The discharge potential for the electrolysis of cobalt in 0.28 mol/liter solution of ammonium oxalate at all the temperature we studied was more positive than in the electrolysis of the 0.21 mol/liter solution. Only at ~100°, when there was no decomposition of xalate to carbon, was the discharge potential of cobalt more negative than in its electrodeposition from 0.21 mol/liter buffer solution.

Thus the optimum conditions of electrolysis of cobalt should be taken as ~0.20 mol ammonium oxalate, pH 4.0 and 95-100°.

Rate of electrodeposition of cobalt under optimum conditions. The electrodeposition of cobalt was carried out at a voltage of 1.8 V, exceeding the decomposition potential by 55%. The duration of electrolysis was 60 minutes and cobalt solutions of various concentrations were used (from 0.006 to 0.06 N). The rate of deposition as a function of time is indicated by the experimental results given in Table 3.

In all experiments the deposits obtained were compact, adhered well to the cathode, were lustrous, finely crystallized, and contained no impurities. Polarographic examination of the solution showed that the quantity of cobalt not discharged corresponded exactly to the difference between the quantity of metal introduced into the solution and that deposited as a result of electrolysis. From Table 3 it is evident that at all the concentrations studied the bulk of cobalt was deposited in approximately 40 minutes.

With decrease of the initial concentration of cobalt in the solution, the

rate of electrodeposition of cobalt fell sharply. The remaining thousandth and ten thousandth of a gram of metal separated in the course of a fairly long time. At the end of 60 minutes of electrolysis the quantity of cobalt not separated from the solution was of approximately the same order and this small quantity of cobalt requires a fairly considerable time for its deposition. Practically all the cobalt is deposited in 65-70 minutes at 1.8 V and in 50-60 minutes at 1.9 V.

TABLE 3

Variation of Rate of Electrodeposition of Cobalt with Time

Duration of electrolysis of cobalt (in min)	Initial concentration of cobalt, N	Quantity of cobalt separated (g)	Quantity of cobalt separated (%)	Remarks
10	$6 \cdot 10^{-3}$	0.0060	33.70	Initial quantity of cobalt 0.0178 g
20		0 0078	43.80	
40		0.0144	80.90	Cobalt left in solution 0.0006 g
60		0.0172	96.63	
10	$1 \cdot 10^{-2}$	0.0206	69.70	Initial quantity of cobalt 0.0297 g
20		0.0244	82.50	
40		0.0286	96.63	Cobalt left in solution 0.0002 g
60		0.0294	99.32	
10	$6 \cdot 10^{-2}$	0.0865	48.54	Initial quantity of cobalt 0.178 g
20		0.141	79.10	
40		0.170	95.56	Cobalt left in solution 0.0025 g
60		0.1755	98.87	

TABLE 4

Rate of Electrodeposition of Cobalt at an Initial Concentration of 0.06 N

Duration of electrolysis of cobalt (in min)	Quantity of cobalt deposited (in g)	Rate-constant for electrolysis of cobalt, K	Quantity of cobalt remaining in solution (g)	Initial quantity of cobalt (g)
20	0.1408	$7.96 \cdot 10^{-2}$	0.0372	0.178
40	0.1704	$7.96 \cdot 10^{-2}$	0.0076	0.178
60	0.1760	$7.51 \cdot 10^{-2}$	0.0020	0.178

The rate of deposition of cobalt under the conditions given is well characterized by the rate constant of electrolysis, related to a solution the initial concentration of which is 0.06 N (Table 4.)

SUMMARY

1. It has been shown that the basic factors for the rate of electrodeposition the qualtity of the metallic deposit, displacement of the discharge potential and change of the decomposition voltage of cobalt, are the pH and temperature of the solution. The optimum conditions for the electrolysis of cobalt are: pH 4, temperature 95-100° ammonium oxalate of concentration~0.20 mol/liter, at a voltage of 1.8

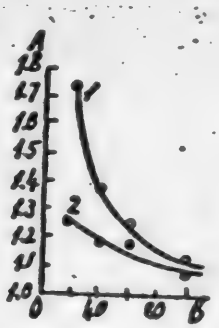

Fig.2. Variation of bath voltage in the decomposition of 6.10^{-2} Co sulfate solution with temperature.
A) decomposition voltage (in V)
B) temperature (in °)
1) 0.21 mol. solution of $(NH_4)_2C_2O_4$;
2) ditto, 0.28 mol.

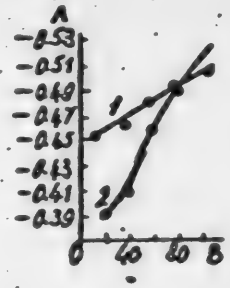

Fig.3. Variation of discharge potential for Co with temperature.
A) discharge potential (in V);
B) temperature (in °)
1) 0.21 mol. solution of $(NH_4)_2C_2O_4$;
2) ditto, 0.28 mol.

2. It has been found that at all temperatures, apart from 95-100°, there is a decomposition of ammonium oxalate to carbon in the electrodeposition of cobalt, which facilitates contamination of the metal.

3. It is note worthy that with increase of the concentration of ammonium oxalate the discharge potential for cobalt becomes more positive, which is apparently connected with the side process of ammonium oxalate decomposition.

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CORROSION OF METALS BY HYDROCARBON SOLUTIONS OF CARBOXYLIC ACIDS

L.G.Gindin and V.A.Kazakova[1]

To complete the investigation of the corrosion processes occurring during the oxidative cracking of gasolines [1-6], we undertook a study of the action on metals of hydrocarbon solutions of certain carboxylic acids.

Very little attention seems to have been paid to this matter in the literature. Matthews (1905) [7] was apparently the first to draw attention to the very destructive action of trichloroacetic acid, dissolved in benzene and kerosene, on metals. However, we did not find any further information about this matter in his paper. Bespolov (1931) [8] investigated the action of decinormal solutions of formic, acetic, propionic, butyric, valeric, caproic, and stearic acids, dissolved in gasoline, , on copper and lead. These experiments of Bespolov's, however, were only exploratory in nature and, in the words of the author himself, need confirmation. He found that, as the molecular weight of the acids increases (from $C_2H_4O_2$ to $C_6H_{12}O_2$) their corrosive power increases. Prutton et al (1945) [9] investigated the corrosion of lead and cadmium by solutions of lauric acid in mineral oil, xylene and benzene as a function of their concentration, temperature, oxygen pressure and other factors. These workers came to the conclusion that the presence of oxygen or of peroxides is necessary for corrosion and that, when stable solvents are used, the quantity of oxygen adsorbed is equivalent to the quantity of metal corroded. The limiting rate of corrosion of lead in solutions of lauric acid dx/dt in the presence of oxygen, and over wide limits of acid concentration, can be expressed by an equation of the type $dx/dt = kP$ where the dependence of the constant k on the temperature is:-

$$\log_{10} k = -\frac{A}{T} + C.$$

Like Denison (1944) [10], Prutton et al maintained the view that the process of corrosion of lead and cadmium in the solutions mentioned, occurs in two stages:

$$2\,Me + O_2 \rightarrow 2\,MeO,$$

$$MeO + 2RCOOH \rightarrow Me(RCOO)_2 + H_2O.$$

The rate of corrosion of lead in benzene and xylene solutions of lauric acid, in the presence of oxygen, at temperatures of 50-60° is limited by the rate of oxidation of the metal, and at temperatures between 60 and 70° by diffusion of O_2 through the insoluble film of lead soap, and above 70° by the diffusion of oxygen through the liquid diffusional layer. Although in the absence of acid no corrosion was visible in pure solvents, none the less its rate was limited more by the diffusion of oxidant to the metal and by the reaction of the one with the other, than by the concentration of the acid. Experiments on the corrosion of lead at 80-100° by solutions of lauric acid in mineral oil and xylene showed, in the words of Prutton et al, that the concentration of acid (which was varied over the fairly

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[1]) Communication VIII of a series in the field of the corrosion of metals by non-electrolytes.

wide range of 0.04 - 0.25 mol/liter, has only a small effect on the rate of the process. In benzene and xylene solutions the corrosion of lead proceeds at the same rate, while in mineral oil its rate is ten times slower on account of the greater viscosity of this oil. Finally from experiments on xylene solutions of lauric acid it emerged that the rate of corrosion of lead was little affected by the moisture content of the solution. In the absence of oxygen or peroxides, lead was not observed to corrode in solutions saturated with moisture even at 100° while in the presence of oxygen the rate of corrosion by moist solutions was somewhat less than that by dry solutions. The behavior of cadmium was, in all essentials, identical with that of lead.

The treatment of the corrosion processes by Prutton et al, who described them as "purely" chemical processes proceeding exclusively through oxide formation, is not in accordance with the facts as we attempt to show in another paper.

In order to accumulate experimental material relative to the processes of corrosion of metals by hydrocarbon solutions of carboxylic acids, we undertook the investigation of the action of acetic, propionic, n-valeric, and n-caproic acids in isooctane, benzene and petroleum ether on magnesium, iron and lead.

EXPERIMENTAL

Method of investigation. The composition of the metals studied is set forth in Table 1; the physical constants of the acids and solvents in Tables 2 and 3.

The solvents were carefully dried with sodium and were then distilled from it into the flasks in which the solutions were prepared. The experiments were carried out in test tubes closed with treated corks[1] from hooks in which the pieces of metal (2x20x60mm) were suspended, completely immersed in the solution. The test tubes were set aside at room temperature in diffused light, usually for about 10 days, after which the solutions were titrated and the losses of metal determined. Comparison of the quantity of reacted metal and acid gave in the majority of cases, a determination of the composition of the corrosion products, which had a considerable significance for the characteristics of the processes studied.

TABLE 1

Chemical Composition of the Metals Examined

Metal	Cu	Mn	Si	Fe	Bi	Zn	C	P
Magnesium	–	–	Traces	0.09	–	–	–	–
Iron	–	0.31	0.19	–	–	–	0.21	0.15
Lead	0.08	–	–	0.06	0.11	0.14	–	–

Corrosiveness of the acids as a function of molecular weight: The action of ~0.5 N isooctane solutions of acetic, propionic, n-valeric and n-capr. acids on magnesium showed that the corrosiveness of the acids under the conditions described increased in going from the lower to the higher homologs. The loss of magnesium in solutions of caproic and valeric acids was 4 times higher than the loss in propionic acid and 8 times that in acetic acid solutions. (Table 4).

Corrosion of metals by solutions of acids having different concentrations: it emerges from the data of Tables 5 - 11, in particular, that the dependence of the extent of corrosion on the acidity of the solution depends on the metals and acids involved.

[1]) This, however, did not prevent access of atmospheric oxygen, necessary for the progress of the corrosion.

TABLE 2

Constants of the Carboxylic Acids Investigated

Acid	D_4^{20}	B.p./ 750 mm Hg (in °)	B.p./ 28 mm Hg (in °)	Freezing point (in °)	Melting point	Remarks
Acetic	1.04926	116.0		16.85		"Limited purity" preparations synthesized by IREA at special request
Propionic	0.99340	141.0		-21.7	-21.7	
n-Valeric	0.93906	186.3		-33.8	-33.8	
n-Caproic	0.92715	205.0	119.5	- 3.8	- 3.8	
Chemically pure glacial acetic[1].	1.0485	116-116.5				Repeatedly frozen out and re-distilled

1) The majority of the experiments were carried out with "limited purity" acids and only a few with chemica ly pure CH_3COOH.

If the dependence of the loss of metal ρ on the concentration C of the solutions is expressed by an equation of the type $\rho = a \cdot C^n$, then $n>1$ for the case of Fe-CH_3COOH, Mg-CH_3COOH and Mg-CH_3CH_2-COOH and $n<1$ for the corrosion of Mg in solutions of $CH_3(CH_2)_4COOH$ and of Pb-CH_3CH_2COOH.

The loss of Pb in 1.44 N solutions of caproic acid did not exceed its loss in 0.54 N solutions (Table 10).

TABLE 3

Characteristics of the Solvents Investigated

Solvent	D_4^{20}	B.p./ 765 mm (in °)	Remarks
Isooctane	0.700	97—99	Technical product
Benzene	0.874	80.5	
Petroleum ether	0.712	60—80	

Further examination of the data shows that in the various solutions, salts of different compositions are formed, depending on the nature of the hydrocarbon and the acids and, (which needs emphasis), on the concentration of the latter in the solution.

In this connection let us turn our attention to the composition of these salts. Judged by the relative quantity of reacting metal and acid, in the corrosion of magnesium in benzene solutions of acetic acid, the neutral salt $Mg(CH_3COO)_2$ is obtained (Table 5). On the other hand, in the corrosion of the same metal in isooctane solutions of acetic acid, an acid salt is formed: $Mg(CH_3COO)_2 \cdot 2CH_3COOH$. In these cases the composition of the salt does not depend upon the concentration of the acid (Tables 5 and 6). In the corrosion of magnesium and lead in isooctane solutions of propionic and caproic acids (Tables 7-10) the composition of the salts was, on the other hand, determined by the concentration of the solutions. In low concentrations the normal salts, $Me(R \cdot COO)_2$, were obtained and in strong solutions acid salts having the composition $Me(R \cdot COO)_2 \cdot n\text{-}RCOOH$. When the molecular weight of the acid was raised, the solubility of the acid salt in isooctane increased. Starting with an almost zero solubility of the acid acetates and a very weak solubility of the acid propionates we found a comparatively high solubility for the acid caproates.

TABLE 4

Corrosion of Magnesium in 0.5 N Isooctane Solutions of Carboxylic Acids

Duration of experiments 66 hours; 50 ml of solution in each test tube

Acid	Loss of magnesium (in g) in different experiments				Loss of acid (in g) in different experiments			Composition of the salt formed
	No.1	No.2	No.3	Average loss	No.1	No.2	No.3	
Acetic	0.0098	0.0096	0.0104	0.0099	0.094	0.100	0.094	$Mg(CH_3COO)_2 \cdot 2CH_3COOH$
Propionic	0.0220	0.0218	0.0220	0.0219	0.136	0.136	0.136	$Mg(CH_3CH_2COO)_2$
n-valeric	0.0880	0.0718	0.0910	0.0836	Could not be determined on account of the dissolution of the corrosion products			
n-Caproic	0.0896	0.0724	0.0886	0.0835	ditto			

TABLE 5

Corrosion of Magnesium by Benzene Solution of Acetic Acid[1]

Duration of experiments 33 days; 80 ml of solution in each test tube

Loss of magnesium	Loss of acid	Loss of magnesium	Loss of acid	Remarks
Concentration of initial solution				
2.05 N		0.25 N		
1.0341	5.4	0.0108	0.05	White crystalline deposit on the magnesium sample
1.2303	6.2	0.0162	0.07	
1.0574	5.6	0.0242	0.13	
1.107		0.017		
Concentration of initial solution				
0.94 N		0.12 N		
0.1355	0.76	0.0078	0.040	Salt formed corresponding to the formula $Mg(CH_3COO)_2$
0.1376	0.76	0.0116	0.060	
0.1360	0.76	0.0166	0.10	
0.136		0.012		
Concentration of initial solution 0.5N				
0.0288	0.12	-	-	
0.0528	0.23	-	-	
0.0522	0.27	-	-	
0.045				

1) In this and subsequent tables the averages of the figures set out are given in the first columns.

TABLE 6

Composition of Salts Formed in the Corrosion of Magnesium by Isooctane Solutions of Acetic Acid

Loss of magnesium	Loss of acid	Remarks
Concentration of initial solution 1.99 N		
0.3476	2.91	Experiments carried out under different conditions, as a result of which it is not possible to compare the characteristics of the dependence of corrosion on the concentrations of the acid in solution. In all cases a salt corresponding to the formula $Mg(CH_3COO)_2 \cdot 2CH_3COOH$ was formed.
0.4282	3.66	
0.4086	3.59	
Concentration of initial solution 0.99 N		
0.1542	1.24	
0.1500	1.10	
Concentration of initial solution 0.57 N		
0.0098	0.09	
0.0096	0.10	
0.0104	0.09	
Concentration of initial solution 0.10 N		
0.0018	0.018	
0.0014	0.018	
0.0016	0.018	

However, the acid caproates dissolved in isooctane better, the more free acid they contained. It is possible that this can explain the similar losses of lead in 0.54 and 1.44 N solutions of caproic acid (Table 10), in spite of the complete solubility of the acid caproate and the exposure of the metal surface as a result of this. It may be supposed that this does not increase the corrosion in these cases, and that the conversion of the neutral to the acid salts, and the solution of the latter in isooctane, leads to a "binding" of comparatively large quantities of acid so that the solutions become impoverished in acid, capable of interacting with metal.

It is interesting that in solutions of acetic acid in isooctane, the corrosion of iron proceeds with the formation of neutral ferrous acetate $Fe(CH_3COO)_2$ under the influence of atmospheric oxidation (Table 11).

Thus the character of the salts formed in corrosion depended in our experiments on the metal, the hydrocarbon solvent, the molecular weight and concentration of the acid in the solution.

Effect of nature of solvent on the corrosiveness of acid solutions. Comparison of the action of acetic acid, in benzene and petroleum ether[1] (Tables 12 and 13 on magnesium shows twice as large an attack on magnesium in the ether solution than in the benzene for apparently similar corrosion in both solutions.

[1]) On account of the shortage of isooctane we replaced it by petroleum ether, whose use we had stopped because, in the corrosion of magnesium in petroleum ether and benzene solutions of acetic acid, neutral acetates are formed, (while acid acetates are formed in isooctane solutions).

The corrosion rates were higher in the first moments of corrosion, judged by the change of acidity, and decreased considerably with time, in all probability as a result of the obstruction of the surface of the metal by the products of corrosion. Weak flashes of corrosion, occurring after almost complete ending of corrosion, (44-148 hours), indicated a new penetration of acid through layers of acetate previously not penetrated.[1]

TABLE 7

Corrosion of Magnesium by Isooctane Solutions of Propionic Acid
Duration of experiments 40 days; 50 ml solution in each test tube

Loss of magnesium (in g)	Loss of acid (in g)	Remarks
Concentration of initial solution 1.4 N		
0.4284	2.93	The plates of magnesium, shining as though polished, covered with an adherent transparent glassy deposit. A small quantity of the corrosion product (0.04 g) was found in solution. The composition of the salt formed corresponded to $Mg(CH_3CH_2COO)_2$ with a mixture of $Mg(CH_3CH_2COO)_2 \cdot 2CH_3CH_2COOH$
0.4118	2.93	
0.4116	3.02	
0.417		
Concentration of initial solution 1.0 N		
0.1956	1.44	
0.1980	1.65	
0.1960	1.16	
0.196		
Concentration of initial solution 0.54 N		
0.0708	0.43	On the samples of magnesium, shining as though polished, a white finely crystallized deposit. Composition of the salt formed corresponded to $Mg(CH_3CH_2COO)_2$.
0.0718	0.47	
0.0706	0.43	
0.071		
Concentration of initial solution 0.25 N		
0.0232	0.08	
0.0230	0.10	
0.0208	0.10	
0.022		
Concentration of initial solution 0.08 N		Surface of the sample obscured by coarse white crystalline deposit. The same coarse deposit on the walls of the test tubes. Composition of the salt formed corresponded to $Mg(CH_3CH_2COO)_2$.
0.0078	0.04	
0.0086	0.05	
0.0080	0.04	
0.008		

See next page for footnote[1])

TABLE 8

Corrosion of lead by isooctane solutions of propionic acids

Duration of experiment 40 days; 50 ml of solution in each test tube

Loss of magnesium (in g)	Loss of acid (in g)	Remarks
Concentration of initial solution 1.4 N		The plates of lead, strongly corroded, were covered by deep corrosion pits. After washing with alcohol the plates had an unusual shiny appearance. On the bottom of the test tubes there was a thick layer of transparent, colorless, thick liquid. Some time after the ending of the experiment this liquid usually crystallized. 0.004 g of salt was found in solution. The composition of the salt formed corresponded to a mixture of $Pb(CH_3CH_2COO)_2$ and $Pb(CH_3CH_2COO)_2 \cdot nCH_3CH_2COOH$.
5.4586	4.92	
5.3112	4.85	
5.5940	4.85	
5.452		
Concentration of initial solution 1.00 N		
3.3770	3.25	
3.6337	3.43	
3.3326	3.22	
3.448		
Concentration of initial solution 0.53 N		Transparent crystals of salt. No layer of heavy liquid. Composition of salt corresponded to the formula $Pb(CH_3CH_2COO)_2$.
2.5908	1.96	
2.0524	1.64	
2.2480	1.74	
2.297		
Concentration of initial solution 0.25 N		
1.3622	0.91	
1.1672	0.82	
1.3104	0.91	
1.279		
Concentration of initial solution 0.08 N		
0.4874	0.29	
0.4850	0.29	
0.4842	0.29	
0.4855		

Effect of water. In order to elucidate the effect of water dissolved in the hydrocarbons, on the corrosiveness of the solutions of acids we carried out a series of experiments with magnesium immersed in solutions of acetic acid in dry and moist petroleum ether. These experiments showed that the moisture has

[1]) By distributing the substance between two non-miscible solvents [11] one of which was water, in which the acetic acid is monomeric, we determined the molecular state of CH_3COOH in petroleum ether, isooctane and benzene, to be dimeric in all three cases.

TABLE 9

Corrosion of magnesium in isooctane solutions of caproic acid

Duration of experiments 40 days; 50 ml of solution in each test tube

Loss of magnesium (in g)	Loss of acid (in g)	Remarks
Concentration of initial solution 1.44 N		
0.4356 0.3886 0.410	Could not be determined by titration on account of the dissolution of products of corrosion.	Product of corrosion evidently magnesium acid caproate, found entirely in solution. Solution remained transparent.
Concentration of initial solution 0.54 N		
0.3028 0.2820 0.2896 0.291	Could not be determined by titration on account of the dissolution of products of corrosion.	Plates were covered with a voluminous gelatinous precipitate. 0.25 g of salt found in solution
Concentration of initial solution 0.10 N		
0.0596 0.0598 0.0642 0.061	0.60 0.60 0.60	On the metal, and in the solution, the same sort of deposit, only in smaller quantity. No salt dissolved in the solution. Composition of the salt $Mg[CH_3(CH_2)_4COO]_2$

absolutely no influence on the rate of corrosion. The loss of magnesium in solutions containing water (Table 14) was no greater than the loss in anhydrous solvent (Table 13). This confirms once again the fact that water, dissolved in hydrocarbons in quantity insufficient to form a new phase, does not raise the corrosiveness of solutions of acids in them.

According to Patten [12], and also Prutton et al [9], moist hydrocarbon solutions of acids are less aggressive than dry solutions. Water becomes corrosive only when it forms a second phase. The aqueous phase of such a two phase system is naturally aggressive and metals placed in it are subject to corrosion, which is particularly intense at the zone of contact between the two phases. The corrosion of metals in such heterogeneous systems has been studied in detail by one of us in a series of papers [13-15].

TABLE 10

Corrosion of lead by isooctane solutions of caproic acid

Duration of experiments 40 days; 50 ml of solution in each test tube

Loss of magnesium (in g)	Loss of acid (in g)	Remarks
Concentration of initial solution 1.44 N		
1.3396 1.0776 1.2101 1.209	Could not be determined by titration on account of the dissolution of products of corrosion	Plates had a polished appearance. The corrosion product was probably entirely lead acid coproate, completely dissolved in the solution, which remained transparent.
Concentration of initial solution 0.54 N		
1.2076 1.2770 1.1330 1.206	Could not be determined by titration on account of the dissolution of products of corrosion	On the lead, and on the bottom of the test tubes, colorless, coarse crystals. Only about 0.1 g of salt in solution.
Concentration of initial solution 0.10 N		
0.6728 0.6632 0.6728 0.669	0.60 0.60 0.60	The surface of the plates covered with a thin, white, slightly rough deposit. No salt in solution. Composition of the salt formed corresponded to $Pb[CH_3(CH_2)_4COO]_2$

TABLE 11

Corrosion of iron by isooctane solutions of chemically pure acetic acid

Duration of experiments 44 days; 90 ml of solution in each test tube

Loss of magnesium (in g)	Loss of acid (in g)	Remarks
Concentration of initial solution 1.0 N		
1.2224 1.2062 1.2916 1.240	2.5 2.6 2.7	Two layers of corrosion products on the iron plates. The outer thin, light layer consisted entirely of ferric oxide. The inner, dense layer consisted of ferrous oxide compounds. The composition of the salt formed corresponded to $Fe(CH_3COO)_2$
Concentration of initial solution 0.5 N		
0.4855 0.4976 0.4558 0.479	1.09 1.10 1.09	
Concentration of initial solution 0.26 N		
0.1348 0.1462 0.1322 0.137	0.34 0.35 0.30	A brown deposit on the plates, of ferrous and ferric compounds. The composition of the salt the same as above

Table 11 continued on page 1098

Table 11 continued.....

Loss of magnesium (in g)	Loss of acid (in g)	Remarks
Concentration of initial solution 0.14 N		
0.0192		
0.0212		
0.0198	Average	
0.020		
Concentration of initial solution 0.07 N		
0.0026		
0.0008		
0.0018	Average	
0.002		
		On the surface of the plates dispersed fine corrosion pits; the corrosion product was composed of ferrous and ferric iron compounds.

TABLE 12

Corrosion of magnesium in benzene solutions of acetic acid

Duration of expt. (in hrs)	Experimental results No.1	No.2	No.3	Mean value	Loss of acidity (in mg KOH)	(In g of acid)	Remarks
	Acidity (in mg KOH)						
0	8832.8	8332.8	8332.8	8332.8	0	0	100 ml of solution placed in each test tube. At known time intervals the acidity of the solutions was determined, from which the progress of the corrosion could be assessed. The salt formed corresponded to the formula $Mg(CH_3COO)_2$
2	8080.8	8080.8	8080.8	8080.8	252.0	0.270	
5	8080.8	8080.8	8080.8	8080.8	252.0	0.270	
48	7817.6	7817.6	7817.6	7817.6	515.2	0.534	
144	7812.0	7812.0	7812.0	7812.0	520.8	0.558	
216	7761.6	7789.6	7716.8	7756.0	576.8	0.618	
336	7666.4	7722.4	7666.4	7685.0	647.8	0.694	
	Loss of magnesium (in g/336 hours)						
	0.1986	0.1844	0.2064	0.1965	—	—	

TABLE 13

Corrosion of magnesium by solutions of acetic acid in petroleum ether

Duration of expt. (in hrs)	Experimental results No.1	No.2	No.3	Mean value	Loss of acidity (in mg KOH)	(In g of acid)	Remarks
	Acidity (in mg KOH)						
0	8332.8	8332.8	8332.8	8332.8	0	0	100 ml of solution in each test tube. At known intervals of time the acidity of the solutions was determined, from which the course of the corrosion could be assessed. The salt formed corresponded to the formula $Mg(CH_3COO)_2$
2	7873.6	7873.6	7924.0	7890.4	442.4	0.474	
5	7805.2	7805.2	7805.2	7805.2	527.6	0.566	
48	7364.0	7414.4	7414.4	7397.6	935.2	1.000	
144	7364.0	7414.4	7414.4	7397.6	935.2	1.000	
216	7044.8	7224.0	7044.8	7106.5	1226.3	1.314	
336	6473.6	6843.2	6770.4	6695.7	1637.1	1.754	
	Loss of magnesium (in g/336 hours)						
	0.3610	0.3134	0.4078	0.3607	—	—	

TABLE 14

Corrosion of magnesium by solutions of acetic acid in petroleum ether, saturated with water

Duration of expt. (in hrs)	Experimental results				Loss of acidity		Remarks
	No.1	No.2	No.3	Mean value	(in mg KOH)	(in g of acid)	
0	8360.8	8360.8	8360.8	8360.8	0	0	Petroleum ether was shaken up in a separating funnel with water. The water was decanted, and the clear transparent petroleum ether used to dissolve 'limited purity' acetic acid. As a control, petroleum ether, dried over sodium, was used (Table 13). See Table 13 for remarks about the composition of the salt and corrosion products
2	7974.4	7999.4	7994.4	7981.6	379.4	0.406	
5	7924.0	7924.0	7924.0	7924.0	436.8	0.467	
48	7414.4	7436.8	7414.4	7455.3	905.5	0.970	
144	7291.2	7414.4	7392.0	7365.9	994.9	1.065	
216	6792.8	7140.0	7140.5	7024.5	1336.3	1.431	
336	6568.8	6893.6	6619.2	6695.7	1666.9	1.786	
Loss of magnesium (in g/336 hours)							
	0.3798	0.3464	0.3706	0.3656	—	—	

SUMMARY

1) The corrosiveness to magnesium of isooctane solutions of the acids investigated, increases with increase in the molecular weight of the acid.

2) The corrosion of magnesium, iron and lead in solutions of acetic and propionic acids, and magnesium in solutions of caproic acid, increases with increase in the acidity of these solutions. The loss of lead in 1.5 N solutions of caproic acid does not exceed the loss suffered by the same metal in 0.5 N solution.

3) The character of the salts formed during the process of corrosion, depends on the nature of the metal, on the properties of the hydrocarbon solvents, - benzene, isooctane, and petroleum ether, and also on the molecular weight of the acids and their concentrations. Depending on the factors mentioned, either a neutral salt $Me(RCOO)_2$, or the acid salt $Me(RCOO)_2 \cdot nRCOOH$ was obtained.

4) With increase of molecular weight of the acid the solubility of the acid salt in isooctane increases. The solubility of the acid acetates is practically zero, that of the acid propionates is very weak, but that of the acid caproates is comparatively large.

5) Acetic acid in petroleum ether is much more aggressive to magnesium than when dissolved in benzene.

6) Solutions of acetic acid in petroleum ether, saturated with water, are no more aggressive than solutions of the same acid in anhydrous petroleum ether.

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INVESTIGATION OF THE EFFECT OF ADDITIONS OF SODIUM COMPOUNDS ON THE SEMICOKING OF COAL

M. B. Ravich, V. A. Lanin and V. I. Korshunov

The industrial semicoking of solid fuel developed in response to demands of consumers for products of the thermal decomposition of coal. Before the development of the petroleum refining industry, coal was semicoked to get liquid fuel for illumination. The solid residue was used as a domestic fuel. Later on the process of semicoking solid fuel was carried out on a comparatively limited scale, because the main interest was in the coking of coal to obtain metallurgical coke. In recent years a new interest has arisen in semicoking, from which a primary tar can be obtained, very valuable for chemical treatment. Naturally, the semicoking industry can only be developed on the basis of the complete utilization of all the products obtained in the process. Semicoking gas is of considerable interest for the gas supply of a number of towns and industrial centers, and likewise as a raw material for chemical industries. The solid carbonaceous residue obtained in the process of semicoking provides a smokeless fuel for electric power stations, industry, transport and domestic use. Work on the low temperature treatment of solid fuel has in large part dealt with determining the optimum conditions for semicoking and for treating the primary tar to obtain the largest yield of liquid products.

The addition of various substances with a catalytic action, which has attained wide use in the industrial treatment of petroleum, has scarcely been studied in its application to semicoking. There are only individual reports that some mineral additions to fuel undergoing semicoking cause a change in the yield and composition of the semicoking products.

Several investigations on the reactivity of solid fuel, carried out in the Fuel and Combustion Laboratories of the Energetics Institute of the USSR Academy of Sciences, have shown that the addition of some sodium compounds to fuel before semicoking it, not only changes the quantitative relationship between liquid and gaseous products, but also causes a change in their qualitative composition and the formation of a more active semicoke. The latter circumstance is of considerable interest, because the activated semicoke obtained in this way may find wide use as a high-quality smokeless fuel for domestic use and for other purposes. Thus, for example, activated semicoke is a valuable fuel for transport gas generators, because it raises the output of the gas generators and the calorific value of the gas, or presents the possibility of conducting the gasification process at a lower temperature, which makes the flexible control of the gasification possible; this is necessary for the exploitation of transport gas generator installations.

In our communication we present the results of investigating the semicoking of Zhurinsk coal with additions of NaOH, Na_2CO_3 and NaCl, and of coal from the Chernogorsk region on addition of Na_2CO_3.

EXPERIMENTAL

Coal was ground to 2 mm and impregnated with 10% solutions of the reagents indicated after which it was dried to the initial moisture content and subjected to thermal decomposition. The additions were made in quantity of about 2 wt % on

the dry coal. The investigations were carried out in a laboratory installation, the lay-out of which is shown in Figure 1.

The coal, after suitable preparation, was introduced into an electrically heated retort. Primary tar condensed in flask 2, placed in a vessel 3 filled with a cooling mixture. To eliminate the possibility of particles of low boiling oil being carried over with the gas stream a water condenser 4 was provided. Gaseous petrol was washed out in an absorption vessel 6, filled with solar oil with an initial boiling point of 220°. The primary gas was collected in a calibrated vessel 7 filled with a saturated solution of sodium chloride.

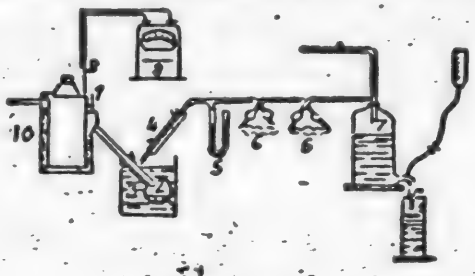

Fig.1. Lay-out of laboratory apparatus for semicoking coal.
1) Fischer retort; 2) wurtz flask; 3) vessel containing cooling liquid; 4) condenser; 5) water manometer; 6) absorption tubes; 7) gasometer; 8) thermocouple; 9) galvanometer; 10) electric furnace.

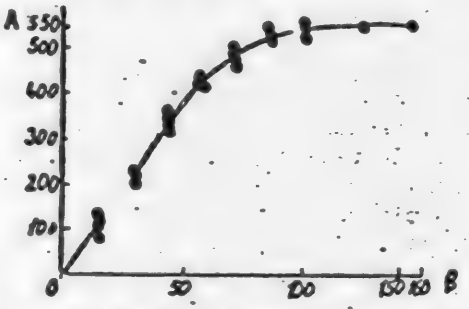

Fig.2. Rate of rise of temperature in semicoking.
A) Temperature in °; B) time (in min).

The maximum temperature of semicoking was taken as 525°. The rate of rise of temperature followed a graph as shown in Figure 2.

The primary tar obtained by thermal decomposition of the coal was distilled into the fractions: <170°, 170-230°, and 230-300°. In each fraction the phenols, bases and neutral oils were determined.

Results of semicoking Zhurinsk coal. The yield of products of semicoking of Zhurinsk coal with and without additions of NaOH, Na_2CO_3 and NaCl are set forth in Table 1.

Comparison of the results obtained shows that addition of 2% NaOH to the coal before semicoking causes a considerable increase in the yield of gas and of gaseous gasoline with simultaneous decrease of the yield of primary tar and of pyrogenetic water. The yield of gas from semicoking the coal without NaOH was 73.4 m^3/t, and with NaOH it was 87.8 m^3/t, i.e., it was raised by 19.7%. The yield of gaseous petrol increased from 0.11 to 0.35%, i.e., more than three times.

The introduction of additions of Na_2CO_3 likewise caused an increase of gas and gaseous gasoline yield, but the catalytic effect of 2% Na_2CO_3 was lower than that obtained with the same quantity of NaOH. However, in this case the gaseous gasoline yield approached 0.23%, i.e. it was twice as large as in the control experiments, and the yield of primary gas increased to 78.34 m^3/t, i.e., by 7%.

Introduction of NaCl caused a small change in the yield of the semicoking product. The yield of primary tar and of pyrogenetic water somewhat increased, but the yield of gas and gaseous gasoline diminished by comparison with the yield of these products obtained by semicoking the initial coal. All this shows that

TABLE 1

Effect of additions on the yield of products of semicoking of Zhurinsk coal

Name of addition	Density of anhydrous tar	Yield (in % on dry coal)				Yield of gas
		Semicoke	Anhydrous tar	Gaseous gasoline	Pyrogenic water	
NaOH.....	1.001	74.5	7.80	0.35	6.30	87.8
Na_2CO_3....	1.033	74.5	8.42	0.22	7.09	78.3
NaCl.....	1.046	75.2	8.95	0.04	7.81	64.1
Without additions	1.037	74.0	8.78	0.11	7.70	73.4

the action of NaCl on the semicoking of coal is different from that of Na_2CO_3.

It is important to note also that the density of the primary tar obtained by semicoking coal with additions of NaOH and Na_2CO_3 is lower than the density of tar from the initial coal, but addition of NaCl causes the density of the tar to increase.

The results of distillation of the primary tar given in Table 2 are of undoubted interest.

TABLE 2

Effect of Additions on the Fractional Composition of Primary Tar from Zhurinsk coal

Addition	Yield of fraction (in % on tar) at the temperatures shown (in °)				Loss (in weight %)
	up to 170	170-230	230-300	Residue	
NaOH	7.90	30.20	12.40[1]	49.20	0.29
Na_2CO_3	7.46	29.00	14.10[1]	49.12	0.32
NaCl	7.28	16.20	26.14	50.02	0.36
Without additions	7.30	16.12	27.35	49.00	0.23

[1]) Distillation was ended at 280° since above this the tar decomposed.

Examination of Table 2 shows that the yield of fraction boiling below 170° depends very little on the nature of the added substance. The yield of the kerosene fraction which distils between 170 and 230° is considerably raised when coal is semicoked in the presence of NaOH and Na_2CO_3.

On treating coal with NaOH the yield of the kerosene fraction increases from 16.12 to 30.20%, i.e., almost by 88% and on introduction of Na_2CO_3 it increases to 29.00%, i.e., by nearly 80% over that in the control experiment. The increase in the yield of the kerosene fractions on treating coal with NaOH and Na_2CO_3 occurs almost completely at the expense of a lowering of the heavier tar fraction, distilling between 230 and 300°.

Thus, the yield of the kerosene fraction on the addition of NaOH was raised by 14.08% over the yield of the same fraction from the tar of the initial coal, but the yield of the heavier fraction, boiling between 230 and 300° was lowered by 14.95%.

On treating coal with Na_2CO_3 the yield of the kerosene fraction increased

by 12.88% over the yield of the same fraction from the tar of the initial coal, with a 13.25% decrease in the yield of the fraction boiling between 230 and 300°.

Addition of NaCl caused only a small increase in the yield of the fraction distilling between 230 and 300°.

The yield of heavy distillation residue remained constant and did not depend on the nature of the added substance. However, the properties of the residue obtained on distilling tar from coal to which NaOH and Na_2CO_3 had been added differed sharply from those of the residue obtained from tar of the initial coal to which NaCl was added.

The heavy residue from the distillation of tar obtained from coal to which NaOH and Na_2CO_3 was added had a higher ductility (fluidity) and was softer at about 20°.

Analysis of the distillates from these tars obtained in the semicoking of coal in the presence of NaOH and Na_2CO_3 (Table 3) showed a sharp increase in the bases and neutral oils and likewise a considerable lowering of the phenols, which was specially notable in the fractions obtained between 170 and 230° and to a lesser degree in the lighter fractions obtained below 170°. Addition of NaCl had no effect on the composition of the distilled tars, as is shown in Table 3.

TABLE 3

Effect of Additions on the Composition of Products of Distillation of Primary Tars from Zhurinsk Coal

Addition	<170° fraction			170-230° fraction			230-300° fraction		
	Composition of the distillation product of the tar (in %)								
	Phenols	Bases	Neutral	Phenols	Bases	Neutral	Phenols	Bases	Neutral
None	34.80	2.80	62.40	61.16	1.81	37.03	56.50	3.30	40.20
NaOH	23.70	6.30	70.00	40.32	5.53	53.55	43.68	4.40	51.92
Na_2CO_3	26.53	4.41	68.06	48.20	5.30	46.50	50.33	4.20	45.47
NaCl	35.10	3.10	61.80	60.24	1.90	37.86	57.30	2.00	40.70

As can be seen from Table 4 the CO_2 content in the gas increased when these substances were added to the coal: the increase with NaOH was from 14.60 to 25.65%, and with Na_2CO_3 from 14.60 to 19.20%; with NaCl an extremely small increase of CO_2 from 14.60 to 15.00%, occurred.

A similar regularity was observed in the change of the unsaturated hydrocarbons and hydrogen contents, although their absolute values are different. Thus with NaOH, for example the content of unsaturated hydrocarbons increased from 4.03 to 6.20% and that of hydrogen from 5.13 to 8.34%. With Na_2CO_3 the unsaturated hydrocarbons and hydrogen changed from 4.03 to 4.80% and from 5.13 to 6.80% respectively.

It should also be noted that there was a lowering of the methane content, from the initial level (in the absence of additions) of 44.60 to 31.81% in the presence of NaOH, and to 36.85% in the presence of Na_2CO_3. The CO content did not change very much, and such change as occurred (see Table 4) can be explained by some inaccuracies in the analysis.

Results of semicoking of Chernogorsk coal: In Fig. 5. are given the yield and fractional composition of the primary tar obtained by semicoking Chernogorsk coal with and without 2% Na_2CO_3. From these it can be seen that there

is an increase of gas yield from 84.1% without, to 102.0 m^3/t with Na_2CO_3 i.e., an increase of 21.3%.

TABLE 4

Effect of Additions on the Composition of Primary Gas from Zhurinsk Coal

Addition	Composition of primary gas (in %)						
	CO_2	C_nH_m	O_2	CO	CH_4	H_2	N_2 (by difference)
None	14.60	4.03	3.93	11.23	44.6	5.13	16.51
NaOH	25.65	6.20	2.60	10.47	31.81	8.34	14.93
Na_2CO_3	19.20	4.80	3.13	11.46	36.85	6.80	17.76
NaCl	15.00	4.00	3.10	12.05	43.50	5.00	16.90

The composition of the primary gas, as can be seen from Table 6 (obtained as a result of semicoking coal to which Na_2CO_3 had been added), differs by an increase in the unsaturated hydrocarbons, carbon monoxide, hydrogen and carbon dioxide with a lowering of the methane content. The yield of primary tar in semicoking coal with additions of Na_2CO_3 is lowered from 11.83 to 10.09% (Table 5). It is important to mention a sharp change in the specific gravity of the tar: the tar obtained in the absence of Na_2CO_3 had a higher density (d^{20} 1.042); when Na_2CO_3 was added the density of the tar was lowered to d^{20} 0.9824, i.e., it became <1.

TABLE 5

Effect of Additions on the Yield of Products of Semicoking and the Fractional Composition of Primary Tar from Chernogorsk Coal

Addition	Yield of semicoking products (in % on dry coal		Yield of gas (in m^3/t)	Fractional composition of primary tar (in % of initial tar) at temperatures				Loss on distillation (in wt %)
	Semicoke	Tar		170	170-230	230-300	Residue	
Semicoking without Na_2CO_3	74.81	11.83	84.10	4.87	6.88	30.70	56.94	1.24
Semicoking with 2% Na_2CO_3	76.22	10.09	102.00	5.71	12.90	25.40	55.63	0.36

TABLE 6

Effect of Na_2CO_3 on the Composition of the Primary Gas from Chernogorsk coal

Addition	Composition of primary gas (in %)						
	CO_2	C_nH_m	O_2	CO	CH_4	H_2	N_2
Semicoking without Na_2CO_3	20.65	2.99	1.58	9.26	49.90	5.24	10.38
Semicoking with 2% Na_2CO_3	25.00	3.75	1.27	12.95	44.50	6.93	5.60

Comparison of the results of distillation of the primary tar from the separate fractions shows an increase in the yields of the lower fractions. Along with this there is a particularly large increase in yield of the kerosene fraction (by a factor of about 2), this being the fraction boiling between 170

and 230°; the increase is obtained at the expense of a corresponding decrease in yield of the heavier fraction, boiling at 230-300°. It is interesting to note that the pitch, remaining after the distillation of tar obtained in semicoking of coal in the presence of Na_2CO_3 differs considerably in its fluidity from the pitch obtained by distilling tar from coal to which no Na_2CO_3 had been added. From a comparison of the data for semicoke yield it follows that addition of Na_2CO_3 leads to a small increase of this coke. This increase in yield of semicoke is evidently due to the mineral part of the addition.

The experimental data on semicoking of coal, with prior addition of the substances mentioned, makes it possible to assert that the addition of sodium carbonate to Chernogorsk coal, and of sodium carbonate and hydroxide to Zhurinsk coal, promotes a deeper cracking of the liquid and gaseous products of the process. As a result of this there is a lower yield of primary tar, an increased yield of gas and gaseous gasoline, and likewise an increased yield of lower boiling fractions, on distillation of the primary tar, and an increase in the amount of unsaturated hydrocarbons and of hydrogen with simultaneous decrease of the methane content of the primary gas.

SUMMARY

1. Sodium hydroxide is most active as a catalyst for promoting deep cracking, and sodium carbonate is less active.

2. Addition of sodium chloride does not exert much effect on the qualitative composition of semicoking products.

3. Some increase of yield of the primary tar, with simultaneous lowering of the gas and gaseous gasoline yield, shows that the addition of sodium chloride to coal impedes the fission of the hydrocarbon molecules during semicoking.

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STUDY OF THE ALKALINE SCOURING OF COTTON ARTICLES

V.E. Postovtsev

Ivanov Research Institute for the Cotton Industry

In many cases it is necessary to carry out the various operations involved in bleaching, particularly scouring on textiles not as yarn but as finished goods. This applies in particular to closely-woven and heavy textiles, which when treated as yarn suffer irreparable deformation and mechanical damage. The existing methods of scouring textile piece goods are neither economically efficient nor efficacious. The further improvement of methods of alkaline scouring is partially obstructed by the fact that, in recent years, differences of outlook have developed among Soviet textile technologists about the proper way to conduct scouring. The earlier, generally accepted, emulsion theory of scouring according to which the central and most difficult task in bleaching is the removal of the greasy contamination from the fibers by alkali-emulsion treatment, has recently met with serious objections.

We have in mind a series of papers by Viktorov, published in "Textile Industry" and the "Journal of Applied Chemistry", starting in 1936 [1].

In these papers Viktorov established that the extraction of the bulk of the grease from cotton fibers with organic solvents does not confer wettability on them (basic index of the quality of scouring), but that stable capillarity is developed when pectin substances are removed, even though there is no substantial change in the content of other impurities.

Apparently from a suggestion made by W.Faer [2] about the distribution of pectin substances as amorphous connective "particles" of cellulose throughout the thickness of the external layers of the fiber wall , Viktorov came to the conclusion that the development of capillary properties in the fiber should be ascribed to a change of the physical structure of the cellulose (increase of its porosity), produced during the extraction of pectin substances from the thickness of the fiber. This process is difficult, in as far as Viktorov (following Faer) considered that the pectins form, with cellulose, ether-like chemical compounds.

According to Viktorov, since the extraction of grease from cotton in scouring does not have any effect on the capillarity, it is not only unnecessary, but even harmful.

In this interpretation of the essentials of the scouring process it should not be taken that the alkali is the only reagent used for the process, various other reagents, capable of extracting pectin, are used for this purpose, mineral acids among them.

Supporters of the emulsion point of view, in their turn, have endeavored to criticize Viktorov's views; he has defended his hypothesis.

Zakoshchikov and Postnikov [3] showed that the capillarity is directly proportional to the grease content in the fiber.

Investigation of the lowering of the capillarity of bleached textiles after hot drying led Kozlov to the conclusion that this phenomenon should be ascribed to the presence of an unextracted grease which, under the conditions of drying

at 70-80°, flows over the surface of the fibers, losing its previous discrete distribution on the fibers, and conferring on the latter a hydrophobic character.

Voronkov and Kozlov [4], refuting the ideas of Viktorov, quoted the observation of Whistler, Martin and Harris that the pectins in cotton are present as calcium, magnesium, or iron salts and are not bound chemically to cellulose, and they also drew on the results of Andersen and Kerr about the distribution of pectins in the primary walls of the fibers, enabling them to assert that their extraction does not involve an ageing of the physical structure of the fiber.

Recalling experiments by Freyberger, which showed that the addition of a small amount of grease, in the bleaching of fabric, sharply lowers its wettability by water, Voronkov and Kozlov deduced from this and other facts that the presence of grease in the primary walls of the fiber is a decisive factor in its wetting and that the extraction of pectin only facilitates the appearance of capillarity, because in this operation part of the grease is extracted as well.

On the basis of this exposition we came to the conclusion that at present there is no unified view on the essentials of the scouring process. Naturally such a state of affairs does not provide any sound foundation for improvement of the conditions of scouring.

We therefore commenced a more careful study of the dependence of the capillarity of textiles on the amounts of various impurities present in them and on the state of the cellulose fiber, with the idea of thus getting nearer to a solution of the problem of selecting the optimum conditions for scouring cotton fabrics.

Dependence of the Capillarity of Cotton Articles On the Grease Contents.

As already indicated, exponents of the emulsion theory of scouring relate the magnitude of the capillarity of the cotton fabric directly to the degree of extraction of grease contamination from it, this grease being distributed in patches in the primary fiber walls. On the other hand, Viktorov denies this connection; the basis of his argument is the fact that after the extraction of greasy contamination from the fiber with, for example, benzene, with which the degree of extraction is immeasurably higher than with alkaline scouring, the fiber always has an unsatisfactory capillarity. Viktorov, apparently, started from the assumption that the fibers are completely degreased by benzene and that their surfaces are rendered hydrophilic. In such a case it would be natural to assume that the properties of the primary fiber wall have no influence on the development of capillarity, and Viktorov does this, ascribing the development of capillarity to a change of the physical structure of the secondary wall ("aged structure") and representing the capillary uptake of water as occurring through the capillaries of the secondary fiber wall.

Such a deduction would only be well-founded if benzene were completely to extract the greasy contamination from cotton. The complicated composition of cotton grease, and its patchy distribution, is opposed to such an assumption. Some time ago Knecht and Strit [5] showed that cotton fabrics contained more substances soluble in benzene than could be extracted by this solvent in the usual way. They found, for example, that further material was extracted by benzene from cotton after bleaching.

Chilikin showed that the quantity of extract depends on the nature of the solvent used; according to his data, chloroform extracts 0.622%, benzene 0.544% ether 0.487%, gasoline 0.421% of substance; on the other hand, successive extractions with these solvents gave a total extract of 0.66%.

Kettering, Goldthwait and Kraemer [6] also indicated that it is doubtful whether with the aid of a single solvent all the grease can be extracted: the

extraction is strongly assisted by the following succession of solvents:

Ethyl alcohol + chloroform – dry chloroform – diethyl ether – alcohol + diethyl ether – acetone – dry diethyl ether – chloroform – benzene.

These authors also indicated that the subdivision of the cotton article for extraction raised the quantity of the extract by a considerable amount; thus while the quantity of extract prior to subdivision was 0.72%, after subdivision it was 1.12%.

All these data are evidence that when being degreased with benzene, cotton does not part with all its grease, and its surface should remain hydrophobic. Thus, the above-mentioned argument against the emulsion theory of scouring could be refuted on the basis of known facts.

However, it would be desirable to show that, in the case of complete extraction of greasy substances from cotton with the aid of organic solvents, true capillarity is attained and that the capillarity developed can be explained by the state of the exterior walls of the fibers, and not by their internal structure.

The experimental work was devoted to an attempt to increase the capillarity of cotton thread by extracting it with different organic solvents.

EXPERIMENTAL

Samples of soft thread No.65, covered with filter paper were extracted in a Soxhlet successively with decalin, (b.p. 182-183°), isoamyl alcohol (b.p. 128--130), benzene (b.p. 80°), and ether (35°). In these tests the total quantity of extract was 3.15%, but capillarity in the thread was not attained.

In other experiments refined thread No.20, covered with filter paper, was extracted successively with petrol (fraction boiling between 70 and 100°) benzene, toluene, (b.p. 111°), xylene (b.p. 136°) isoamyl alcohol, carbon tetrachloride (b.p.77°) and sulfuric ether. The total quantity of extract was found to be 3.12% on the weight of absolutely dry thread.

The unusually large quantity of extract leads one to speculate about the occurrence of some side processes, accompanying the extraction of impurities by the method described.

Actually, extraction of the ashless paper used with the same solvents gave interesting results: an extract of 1.58% on their weight was obtained and at the same time the weight of the filter paper itself decreased by 1.15%.

It was therefore necessary in the light of this result, whose cause remains unexplained, to dispense with the use of filter paper for enveloping the samples of thread.

Subsequently, refined thread was extracted without a paper wrapping, with the following solvents in succession: petrol, benzene, toluene, isoamyl alcohol, carbon tetrachloride. The quantity of extract was determined for each solvent separately (see table).

The weight of thread decreased in the first experiment by 0.357% and in the second by 0.372%. After extraction the thread showed a small capillarity - 29 mm in 30 minutes.

We see that the decrease in weight of the thread during extraction is considerably less than the quantity of material obtained in the extract. This fact, which is similar to what was observed in the extraction of the filter paper, can only be explained by supposing that, side by side with the extraction of fatty impurities, a change in the cellulose fiber itself takes place, increasing the amount

Results of the Determination of the Quantity of Extract

Solvent	Quantity of extract (in % of the weight of absolutely dry thread)		
	Experiment 1.	Experiment 2.	Mean
Gasoline...	0.42	0.42	0.420
Benzene....	0.06	0.07	0.065
Toluene....	0.03	0.04	0.035
isoamyl-alcohol....	0.30	0.28	0.290
carbon tetrachloride	0.03	0.03	0.030
		Sum	0.840
Benzene (one expt)			0.550

of extract somewhat, and also increasing its own weight, which in the final analysis means a reduction in the loss of weight of the thread as a result of the extraction, and makes this loss in weight less than the weight of the extract formed.

It was later established that in extracting thread with benzene the quantity of extract exactly coincided with the loss in weight of the fibers, indicating the absence of any change of the cellulose in this particular case.

It remains to suggest that the observed non-correspondence between the weights of extract and the loss in weight of the thread on extraction by a number of solvents, the cause of which can only be ascribed to a change in the cellulose itself or of its congeners in the course of extraction, is due to the use of high boiling solvents.

Extraction of thread with benzene.

	Quantity of extract (g)	Loss in weight of cotton (g)
1st expt.	0.0339	0.0339
2nd "	0.0303	0.0309

Thus the task of complete extraction of grease from cotton, in order to make it hydrophilic, by extraction with organic solvents was not achieved: cotton thread did not acquite a sufficient capillarity even on extraction with a number of good grease solvents.

In addition, the use of high boiling solvents for determining the grease content of cotton cannot be recommended, in view of the secondary processes which occur in extraction, and which falsify the results.

It may be asserted that at present the true grease content in cotton is not known, because until now these contaminants have been determined by extraction with organic solvents, and this either does not give complete extraction, or introduces a falsification of the result due to secondary processes.

Dependence of the Hydrophilic Character of the Cotton Fiber on the State of the Primary Fiber Walls.

Experiments to show by direct means that the development of capillarity in cotton articles is directly connected with the presence of fatty substances in the primary walls, (exhaustive extraction), ended in failure.

However, this by no means supports Viktorov's point of view of the negative role of grease in the phenomenon of capillary uptake of water, in so far as the use of organic solvents for extraction simply did not succeed in extracting all

the grease. This only demonstrates the complex composition of cotton grease and the inaccessibility of some of it to the action of solvents on account of the complex structure of the primary walls.

It appeared of interest to get at a solution of the problem indirectly. From among a number of such indirect means, a study of the relation between the hydrophilic character of the cotton fibers and the state of the primary walls was chosen.

The state of the primary walls was changed by mechanical attrition. The cotton staple was lightly pressed on to the surface of a glass slide, fixed to the axis of an electric motor rotating at high speed. The surface of the glass slide was occassionally cleaned with emery paper. Afterwards a drop of water was laid on the surfaces of the initial and the treated staple and the contact angle was measured by projecting an image of the drop on a screen. As a result of a series of such measurements it was found that the contact angle for the initial staple was 132° on the average, while on the staple subjected to mechanical attrition, it was 59.7°.

This is evidence that the hydrophilic, and therefore the capillary, character of the fiber depends on the state of the primary walls: damage to the primary walls and its incomplete repair causes the surface to become more hydrophilic, though the secondary walls remain unchanged in the sense of not being "aged."

As already shown, from the negative role of the primary walls and of the grease contained in them, relative to the capillarity of the cotton fibers (threads, textiles, etc) Prof. Viktorov rather naturally comes to the conclusion that in the capillary uptake of water the latter moves into the system of capillaries of the internal secondary walls, a system consisting of fiber structure "aged" during the process of scouring.

It seemed interesting to test this hypothesis by microscopic examination of the capillary uptake of water on single cotton and other fibers. Isolated cotton or other similar fibers, extracted from well scoured thread were attached by their ends to a stout paper frame. The frame was cautiously glued to an object glass, and this latter was placed on the platform of a microscope, set up vertically. After the lower part of the thread had been brought into focus in the microscope a drop of sodium chromate was laid on the lower part of the frame where the ends of the fibers were located, and the uptake of the colored liquid was observed in the microscope.

As a result of many experiments of this kind it was established that the capillary uptake of water by single fibers is not complete, while in a system composed of 2-3 fibers twisted around each other the rate of uptake was so fast that it could not be observed in the microscope.

SUMMARY

1. The capillary properties of cotton articles are conditioned exclusively by the state of the primary fiber walls.

2. Wettability develops in alkaline scouring with a larger content of grease (left in the material) than when the grease is extracted with grease solvents, a treatment of the fiber with which does not make it wettable. The basic object of scouring appears to be not the simple equilibrium extraction of the greasy impurity by emulsification, but a more or less complete breakdown of the perfection of the external primary walls (cuticle), leading to the creation of a connection between the system of hydrophilic portions and the external surface of the fibers.

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BRIEF COMMUNICATIONS

STUDY OF THE FUSION DIAGRAM FOR THE BINARY SYSTEMS: H_2SeO_4–H_2SO_4; $H_2SeO_4 \cdot H_2O$–$H_2SO_4 \cdot H_2O$ and $H_2SeO_4 \cdot 4H_2O$–$H_2SO_4 \cdot 4H_2O$

A.F.Kapustinsky and A.N.Zhdanova

D.I.Mendeleev Institute of Chemical Technology, Moscow

Sulfur and selenium belong to the sixth group of Mendeleev's periodic system: their oxyacids (sulfuric and selenic) are analogous in composition and therefore it is natural to expect them to be analogous in their crystallochemical relationships. Even a comparison of the fusion diagrams of the systems H_2SeO_4–H_2O and H_2SO_4–H_2O shows that there is a great similarity between them [1].

Khodakov and Agafonova [2, 3] showed that the dissociation constants of selenic and sulfuric acids are very close to each other. The "thermodynamic radii" of the ions SeO_4^{2-} and SO_4^{2-} are, according to Kapustinsky and Yatsimirsky [4], 2.43, and 2.30A respectively.

It appeared interesting to investigate the isomorphism of selenic and sulfuric acids and also of their hydrates.

According to Goldschmidt [5] the general requirement for the isomorphism of substances is that atoms, ions or molecules of isomorphous parts should approximate each other in size and polarization properties. According to Grimm [6] the phenomenon of isomorphism is determined by three conditions: 1) identity of the molecular (stoichiometric) structure of the crystals; 2) approximate equality in size of the structural units of the crystal; and 3) similarity in structure of the elementary cells. The first two conditions are fulfilled for selenic and sulfuric acids because their stoichiometric formulas are identical and the difference between the ionic radii for SeO_4^{2-} and SO_4^{2-} is only 6%. According to the Grimm-Goldschmidt rule, isomorphism (at temperatures not very far removed from those of melting) appears in cases where the radii of the corresponding structural units do not differ from one another by more than 15%.

Thermal analysis is a reliable method whereby the formation or non-formation of solid solutions can be established, and it was therefore selected for the study of the isomorphism of selenic and sulfuric acids.

EXPERIMENTAL

Chemically pure selenic acid was used for the experiments. The method for its production was described earlier [7]. Since there is considerable difficulty in preparing 100% selenic acid we used 97% material; the free water in it was reacted with the calculated quantity of sulfur trioxide, and as a result a mixture of anhydrous selenic and sulfuric acid was obtained. 100% Sulfuric acid was obtained from chemically pure H_2SO_4 in the same way, i.e., by reacting the excess water with SO_3. A solution of sulfuric acid in anhydrous selenic acid was prepared by weighing, precautions being taken against the absorption of moisture from the air by the mixture, since it is extremely hygroscopic.

The monohydrates and tetrahydrates of sulfuric and selenic acids were prepared from more concentrated solutions of acids of known weight, by mixing with an exactly weighed quantity of water to a concentration corresponding to the stoichiometric formula, precautions again being taken against the absorption of

moisture from the air. The solidification point of the mixture was determined in the apparatus described by Kapustinsky and Drakin. The crystallization of the mixture on cooling was induced by the introduction of seed crystals of the pure components.

It should be noted that all the mixtures investigated by us crystallized very much more easily than solutions of selenic acid which did not correspond in composition to those of the hydrates $H_2SeO_4 \cdot H_2O$ and $H_2SeO_4 \cdot 4H_2O$, as a result of which the arrests on the heating curves were obtained extremely accurately and reproducibly. The results of thermal analysis of the system H_2SeO_4-H_2SO_4 are set forth in Table 1 and displayed in Fig. 1, which show that chemical compounds are not formed in this system, and that there is only one eutectic, corresponding to 16% by wt. of selenic acid and solidifying at 3.2°.

As can be seen from the fusion diagrams obtained by us, selenic and sulfuric acids do not form solid solutions, which apparently is due to differences in structure of their elementary cells.

TABLE 1

Fusion Diagram for the system H_2SeO_4-H_2SO_4

Quantity of H_2SeO_4 (wt. %)	Melting point (in °)	Quantity of H_2SeO_4 (wt. %)	Melting point (in °)
0	10.3	50.09	27.3
8.79	7.2	58.65	32.4
11.05	5.5	66.27	38.5
21.82	6.3	76.48	44.5
31.85	13.3	87.20	49.9
41.92	21.3	100.00	56.0[1]

[1]) According to data of Cameron and Macallan [12], and of Kreman [10].

TABLE 2

Fusion Diagram for the system $H_2SeO_4 \cdot H_2O$-$H_2SO_4 \cdot H_2O$

Quantity of $H_2SeO_4 \cdot H_2O$ (wt. %)	Melting point (in °)	Quantity of $H_2SeO_4 \cdot H_2O$ (wt %)	Melting point (in °)
0	9.5	63.41	12.6
13.28	8.5	76.26	15.6
26.41	7.0	85.39	19.0
37.65	5.0	91.01	21.6
48.17	8.0	100.00	24.0
56.90	10.6		

The melting points of mixtures of the monohydrates of selenic and sulfuric acids are given in Table 2. The fusion diagram of the system $H_2SeO_4 \cdot H_2O$-$H_2SO_4 \cdot H_2O$ is displayed in Fig. 2. This diagram is analogous to the preceding one, with a eutectic corresponding to 37.5% $H_2SeO_4 \cdot H_2O$ and at 5°. Thus the monohydrates of selenic and sulfuric acids, like the acids themselves, do not form solid solutions. Since the difference between the radii of the hydrated ions SeO_4^{2-} and SO_4^{2-} should be still smaller than the difference between the radii for the unhydrated ions, we also have to explain the absence of isomorphism between the monohydrates by a difference of structure of their elementary cells.

TABLE 3

Fusion Diagram of the system $H_2SeO_4 \cdot 4H_2O$ – $H_2SO_4 \cdot 4H_2O$

Quantity of $H_2SeO_4 \cdot 4H_2O$		Melting point (in °)	Quantity of $H_2SeO_4 \cdot 4H_2O$		Melting point (in °)
(in wt.%)	(in mol %)		(in wt.%)	(in mol %)	
0	0	-28.8	65.59	59.80	-41.0
11.27	8.93	-30.7	74.35	69.37	-43.3
24.3	20.10	-32.5	83.24	79.62	-45.7
31.41	26.54	-33.6	88.38	85.65	-47.6
47.02	40.98	-37.1	100.00		-50.5
56.09	50.02	-38.8			

The fusion diagram for the system $H_2SeO_4 \cdot 4H_2O - H_2SO_4 \cdot 4H_2O$ is shown in Fig. 3, from determinations of melting points which are given in Table 3.

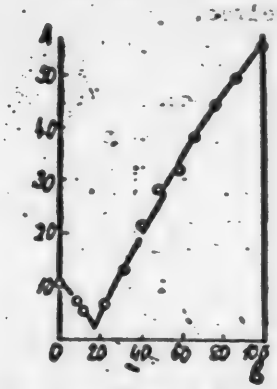

Fig. 1. Fusion diagram of the systems selenic acid-sulfuric acid.

A - temperature (in °)
B - quantity of H_2SeO_4 (in wt. %)

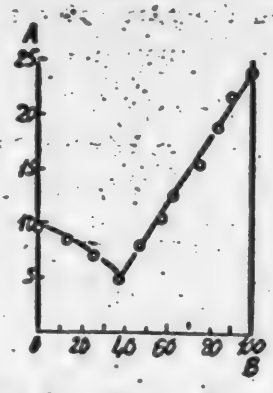

Fig. 2. Fusion diagram for the systems $H_2SeO_4 \cdot H_2O - H_2SO_4 \cdot H_2O$.

A - temperature (in °);
B - quantity of $H_2SeO_4 \cdot H_2O$ (in wt. %)

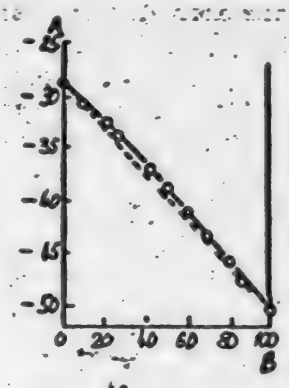

Fig. 3. Fusion diagram for the system $H_2SeO_4 \cdot 4H_2O - H_2SO_4 \cdot H_2O$.

A - temperature (in °);
B - quantity of $H_2SeO_4 \cdot 4H_2O$ (in mol %)

As is shown in Fig. 3, a continuous series of solid solutions is formed here. The approximate linear course of the curve (the true straight line is shown dotted) indicates the absence of interaction between the components and the approximation of the system to an ideal one. It is interesting to note that a similar form of curve has been found in phase diagrams of the system: heavy water-light water [9]. The formation of solid solutions between the tetrahydrates indicates that they are isomorphous.

We note that Kreman and Hofmeyer [10] some time ago studied the composition diagram for the system $H_2SeO_4 - H_2O$ and observed that seeding with crystals of sulfuric acid tetrahydrate caused the solutions of selenic acid, near in composition to the tetrahydrate of selenic acid, to crystallize, which led them to suggest that the tetrahydrates of the two acids are isomorphous. The present work confirms their opinion.

The following explanation of the isomorphism of both acids, as their hydration increases, may be put forward. In spite of the fact that the ionic radii are nearly the same, the difference in structure of the elementary cells is pronounced in the absence of molecules of water of hydration, and this is still true for the monohydrates. However, as the number of molecules of water increases, i.e., as the hydration increases, structural differences begin to play a smaller role, since the molecules of water adhering to the outer layer of the ions have a screening effect. The difference in dimensions of the ions begins to play a more important role. And since, with increase in hydration, the relative difference in radii of these complex ions becomes smaller, the theoretical requirements for the formation of isomorphous solid solutions are fulfilled.

Thus we see that increase of the number of molecules of water of hydration brings the properties of solutions of selenic and sulfuric acids nearer to one another. We thus understand why the dissociation constants of sulfuric and selenic acids, determined by Hamer [11], Agafonova and Khodakov [2,3] are of the same order, since in dilute solutions we have to deal with strongly hydrated ions.

It is natural that the similarity between selenic and sulfuric acids appears to a larger degree in dilute solutions than in concentrated ones, because the radii of the spheres formed by the hydrating molecules of water around the ions differ less than the radii of the ions themselves.

SUMMARY

1. Fusion diagrams for the following systems have been studied:

H_2SeO_4–H_2SO_4; $H_2SeO_4 \cdot H_2O$–$H_2SO_4 \cdot H_2O$; $H_2SeO_4 \cdot 4H_2O$–$H_2SO_4 \cdot 4H_2O$

The first two give curves of the usual eutectic type, but in the third the formation of a continuous series of solid solutionsis indicated. Neither pure selenic and sulfuric acids nor their monohydrates are isomorphous while the tetrahydrates of the acids are isomorphous with one another.

2. The effect of hydration of sulfuric and selenic acids on their capacity for the formation of isomorphous mixtures has been examined theoretically.

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2) See Consultants Bureau English translation, p. 739.

DETERMINATION OF THE HETEROCAPILLARITY OF CLOSELY-WOVEN FABRICS[1]

S.S.Voyutsky and L.E.Peregudova

In the impregnation of textiles with individual liquids and aqueous solutions of emulsifiers, the relation between the diameter of the capillaries and that of the particles of the hydrophobic substances does not arise because the systems involved are molecularly dispersed. The question is different when dispersions are involved. Here, as a result of the large size of the particles of the hydrophobic substances, the process of impregnation may be complicated by phenomena such as the sealing of the passages by which the liquid penetrates into the fabric, and the deposition of the disperse phase on the surface of the fabric by filtration.

The size of the particles of impregnating dispersions has been repeatedly determined. According to Chwala [1], the dimensions of the particles of paraffinic and other dispersions, with which fabrics are usually impregnated to make them waterproof, are 0.1 - 0.2μ. According to Heilman and Chomutova the diameter of the particles of albumenbitumen emulsions, widely used for the manufacture of artificial leather, is 0.98μ, and the maximum diameter does not exceed 4μ. The diameters of the particles in dispersions of synthetic resins usually do not exceed 2μ[2,3]. Synthetic latex, the diameter of the particles of which has frequently been determined, is an ultramicroscopic system, as is well known. This indicates that the diameter of the globules of latex cannot exceed a fraction of a micron. The globules of natural latex can attain quite a large size. According to Lucas [4], the mean diameter of the microscopically visible particles is 1.5μ. If we take into account the ultramicroscopic particles as well, then the average diameter comes out at 0.17μ according to one measurement, and 0.26μ according to another [5]. The particles of artificial dispersions of rubber and reclaim are always considerably larger and can attain a size of 10μ and more [6]. However, this latter system is rarely used for the impregnation of fabrics, and it can in general be said that in the majority of impregnants, the particle size does not exceed 1 - 2μ. While we are more or less clear about the diameter of the particles of the impregnant, the same cannot be said about the size of the capillaries of closely-woven fabrics, usually used to manufacture waterproof materials and artificial leather. No work has recently been devoted to this question, and the size of the capillaries into which the hydrophilic particles of dispersion have to penetrate in order to endow the fabric with water resistance, remains quite unknown.

In the work described below we attempted to determine the distribution curves, showing the number of capillaries as a function of their diameter, for the closest-woven multi-layer material - blanket. The values found permit an assessment, though of a preliminary character, of the sizes of the capillaries into which the dispersion has to penetrate and also makes it possible to say whether the particles of the disperse phase can be filtered out and can obstruct the pores of the fabric during impregnation.

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[1]) Communication II of a series on the process of impregnation of fabrics with aqueous dispersions of hydrophobic substances.

EXPERIMENTAL

A number of methods have been put forward for the determination of the distribution curves for diameters of capillaries in porous systems [7-13]. In the investigation of the heterocapillarity of multi-layer cloth we used the method of Dumansky and Ostrikov [12], as being the simplest and at the same time sufficiently informative. This method is based on the fact that the distribution of liquid with height in porous systems, imbibing liquid from any sort of vessel, depends on the number of capillaries and on their radii.

In its final form, our adaptation of this method for the determination of the heterocapillarity of fabrics was as follows.

A sufficiently long strip of the material being investigated, 1 cm wide, previously marked out in divisions with pencil, was suspended in a vertical glass tube by means of a wire hook, inserted into a cork which closed the upper end of the tube. The lower end of the tube dipped into an Erlenmeyer flask, to such a depth that the end of the strip was immersed to a depth of 2 cm in the liquid which covered the bottom of the flask. Our experiments themselves showed that the most suitable liquid is alcohol, which completely wets cotton fibers. In order to prevent evaporation of the liquid, the neck of the flask was closed with a bung in which there was a hole the size of the tube. The marks on the strip of fabric were carried down to within 2 cm of the lower end of the strip. The distance between two divisions was 10 cm. At the lower end, however, the first two distances between successive marks were 2.5 cm each, and then there was one division of 5 cm.

Fig. 1 gives a general view of the set-up.

After the imbibition of liquid by the fabric had been terminated (in our experiments 7 days was sufficient for imbibition) the apparatus was dismantled, the strip of fabric rapidly removed, cut up into pieces along the divisions, and the pieces weighed.

By simply drying them to constant weight, the amount of alcohol in the pieces was determined (the moisture in the pieces prior to the experiment should be taken into account). The values obtained give the percentage of alcohol at different heights of strip and thus the quantitative distribution of the alcohol in the fabric. Knowing this distribution, and determining from the capillarity law the average radius of the capillaries of different groups (fractions) corresponding to definite intervals of height, the number, cross sectional area, and volume of the capillaries can easily be calculated for each group.

The average radius of capillaries $\underline{r}$ for each group is calculated from the formula:

$$r = \frac{2\sigma}{h \cdot \delta \cdot g},$$

where σ = surface tension of the liquid used for the determination, h = average height of the given division, δ = density of the liquid, g = acceleration due to gravity. The number of capillaries N in each group is calculated from the equation

$$N = \frac{P_n - P_{n+1}}{\pi r^2 \cdot \delta \Delta h}$$

where P_n = quantity of alcohol (in g) in the n-th section of the strip from the initial (lowest) mark; $P_{(n+1)}$ = quantity of alcohol (in g) in the next higher section; Δh = length of the section.

The cross sectional area S of the capillaries of the n-th group, plus the cross sectional area of all the capillaries of smaller diameter was calculated from the following equation:

$$\Sigma S_n = \frac{P_n}{\delta \cdot \Delta h}.$$

Hence the cross sectional area of the capillaries of the n-th group is expressed by the equation

$$S_n = \Sigma S_n - \Sigma S_{n+1}.$$

Since, in the calculation of the cross sectional area of the capillaries, the quantity of alcohol relates to unit length of the fabric strip, it is evident that the volume of the capillaries of each group is numerically equal to the corresponding cross sectional area.

From the data thus obtained, the cross section areas or volumes were easily calculated for each group as a percentage of the total cross sectional area or volume of the capillaries, and in this way a graph of the distribution of pores according to their diameters can be constructed using the generally known graphical procedure.

For investigations with this method, four-layer unshrunk blanket material and two-layer normal material were used, for which the number of threads for warp and weft were respectively 85/3 and 41/3 for the four-layer, and 85/3, 85/3 for the two-layer material. The four-layer material was taken in both the unbleached and the scoured condition. The scouring was done by boiling the fabric for 2 hours with a 20% solution of caustic soda, followed by a thorough washing out of the alkali with water.

Preliminary experiments showed that sufficiently reproducible results could be obtained when working with difference strips taken from one and the same sample of fabric. Further special experiments showed that there was no influence on the results of the direction in which the liquid was imbibed by the fabric. Identical results were obtained with strips suspended either by the warp or the weft, from which it can be concluded that the character of the capillarity is very nearly identical in both directions.

Finally, since the level of the meniscus in the capillaries can be arrived at either by the imbibing of liquid by the capillaries, or by the draining out of liquid from the previously filled capillaries, we carried out experiments with rising and falling liquid. For this purpose, in parallel with experiments by the ordinary method, other experiments were made in which the strips were impregnated with alcohol to complete filling of the capillaries, and the strips were then suspended in the tube. In other respects the method was the same. The results obtained are shown in the Table.

The experiments showed that the capillaries were filled to a higher level by the falling than by the rising method. This is

Fig. 1. General view of the apparatus.

evidently to be explained by the hysteresis which always occurs with such phenomena.

In Fig. 2 are the curves for the distribution of number of pores as a function of their size for four-layer material, constructed from the average data of the Table. It can easily be seen that the most numerous pores are those having a size of 10-30μ. However it can also be seen that there are, in blanket material, many pores of larger diameter. On the other hand there are very few pores with a diameter of less than 10μ.

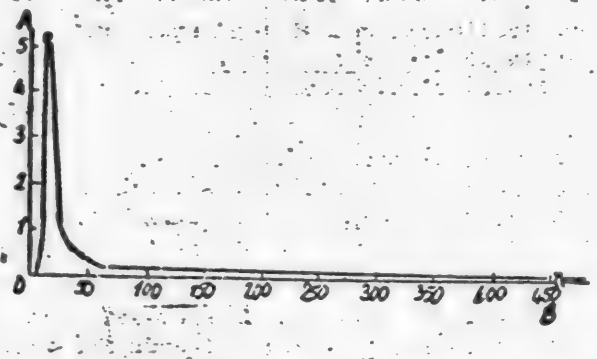

Fig. 2. Curves for the distribution of capillaries in unbleached four-layer blanket material.
$A - \frac{S\ (\text{in } \%)}{\Delta d}$; B - d (in μ).

We similarly carried out experiments for the determination of the quantity and total cross section (volume) of the capillaries of different diameters in unbleached four-layer, scoured four-layer and unbleached two-layer material. These determinations could only be carried out by the imbibing method. Hence the results obtained, presented in the curves of Fig. 3, are not absolute but relative. Examination of them shows that scouring the fabric diminishes the total cross sectional area (and volume) of the coarse capillaries in the fabric but, on the other hand, widens the smaller ones. In another paper [14] we have demonstrated that, in spite of shrinking, scouring causes an increase of the capillary volume of the fabric.

It can be seen from the curves in Fig.2 that those for the two-layer material have the same character as the curves for distribution of pores in the four-layer material. However, according to the results presented in [14] just cited, both unbleached and scoured four-layer blanket material have higher true porosities than two-layer material, indicating that the latter is denser than the former. This is evidently due to the fact that the four-layer material was unshrunk.

Comparison of the sizes of the capillaries of the fabric with the dimensions of the impregnating dispersions shows that, in the impregnation of even the closest-woven multi-layer fabrics, with the usual dispersions of hydrophobic substances, (paraffin, albumen-bitumen, synthetic resin, synthetic and natural latex dispersions) simple blockage of the capillaries or filtering out of the disperse phase is not very probable. This conclusion is supported by the fact that there is no direct connection between the size of the particles of the dispersion and their capacity for impregnation.

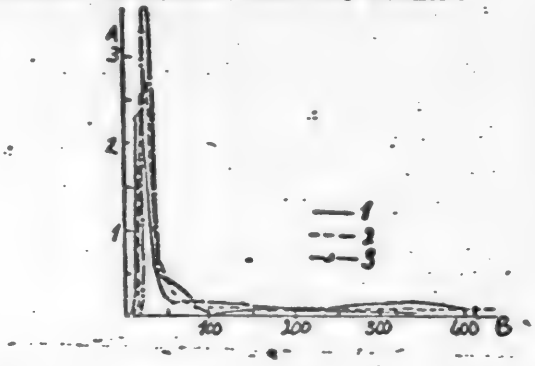

Fig. 3. Distribution curves for capillaries in unbleached four-layer and unbleached two-layer blanket material. A - (in %); B - d(in μ); 1 - unbleached four-layer blanket; 2- scoured four-layer blanket; 3 - unbleached two-layer blanket.

Results of Experiments on the Determination of the Heterocapillarity of Blanket Material

Limiting values of the diameters of capillaries of each group (in μ)	Number of capillaries per 1 cm² cross sectional area						Area of capillary per 1 cm² cross section of the sample					
	Determinations by imbibing (liquid rising)		Determinations by draining (liquid falling)		Average value		Determinations by imbibing (liquid rising)		Determinations by draining (liquid falling)		Average value	
	N	(%)	N	(%)	N	(%)	cm²	(%)	cm²	(%)	cm²	(%)
>461	21	0.05	10	0.01	15	0.03	0.140	18.2	0.062	7.1	0.101	12.2
461-230	312	0.45	154	0.09	232	0.17	0.833	29.8	0.115	13.1	0.144	21.1
230-115	346	0.5	1090	0.5	718	0.5	0.063	8.2	0.200	22.8	0.131	15.9
115-57.6	1083	1.4	1978	0.9	1530	1.1	0.050	6.5	0.092	10.5	0.071	8.6
57.6-38.8	3660	5.1	3420	1.6	3540	2.5	0.062	8.1	0.058	6.6	0.060	7.2
38.8-28.8	4470	6.2	5100	2.4	4780	3.4	0.040	5.2	0.042	4.8	0.041	5.0
28.8-23.0	11230	15.5	8270	3.9	9750	6.8	0.057	7.4	0.042	4.8	0.052	6.3
23.0-19.2	19050	26.3	9930	4.7	14490	10.2	0.066	8.6	0.034	3.9	0.050	6.0
19.2-16.4	20615	28.5	4730	2.2	12673	8.9	0.050	6.5	0.015	1.7	0.033	4.0
16.4-14.4	4680	6.5	23200	11.0	13940	9.8	0.008	1.1	0.042	4.8	0.025	3.0
14.4-12.8	1130	1.5	16200	7.7	8665	6.1	0.0016	0.2	0.023	2.6	0.012	1.4
12.8-11.4	5770	8.0	101000	47.8	53385	37.8	0.0015	0.2	0.123	14.0	0.062	7.5
11.4-10.4	—	—	22600	10.7	11300	7.9	—	—	0.019	2.2	0.010	1.2
10.4-9.6	—	—	13580	6.4	6790	4.8	—	—	0.010	1.1	0.005	0.6
	72367	100.0	211253	100.0	141808	100.0	0.772	100.0	0.877	100.0	0.827	100.0

However this state of affairs would be considerably changed if a dispersion with very large particles were used for impregnation (artificial dispersions of rubber and reclaim, prepared by mastication or by replacement of the solvent, structural latex, irregular preparations of the other types of impregnating dispersions). In these cases when the size of the disperse particles is larger than 10μ, blockage of the capillaries and filtering out of the disperse phase during impregnation will be inevitable.

SUMMARY

1) A comparatively simple method for determining the heterocapillarity of blanket material has been worked out.

2) Using this method, curves for the distribution of pore diameter as a function of number of pores have been obtained for unbleached and for scoured unshrunk four-layer blanket material, and for unbleached two-layer material, and their character has been discussed. It has been shown that in all these forms of the material, the maximum on the distribution curve occurs at 10-30μ. There are many larger capillaries but very few with a diameter less than 10μ.

3) It has been shown that scouring the fabric decreases the number and total cross sectional area of the large capillaries but increases the number of capillaries of small diameter.

4) Since the dimensions of the capillaries are usually considerably larger than those of the particles in impregnating dispersions, it can be concluded that filtering out of the disperse phase or obstruction of the capillaries by particles is only likely if impregnation is carried out with dispersions

containing extremely coarse particles, (with a diameter of the order of 10μ and higher).

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EVALUATION OF BOILER BLOWDOWN AS A METHOD OF COUNTERING FOAMING OF BOILER WATER

S. A. Durov, Ya. M. Nemirovsky and N. G. Fesenko

Hydrochemical Institute of the USSR Academy of Sciences

One of us [1] has established that the foaming of boiler water is due to three causes: presence of inorganic colloids of some optimum degree of dispersion; the attainment of a definite concentration of electrolyte; and the rate of lowering of the pressure of steam over the water. The concentration at which foamy priming in iron vessels reaches half of its maximum value is quite definite, and is different for each electrolyte. In particular, for sodium salts the effect of the sulfate is greater than that of the chloride.

For a mixture of salts, sulfate and chloride, as indicated by Foulk [2] the additivity rule does not apply; our mixture had a greater activity than would be expected from an arithmetical average between the activities of the pure components at the same concentration expressed rationally, i.e., in mg-equiv/liter. Our observation of the effect of colloidal iron hydroxide, a product of the corrosion of the walls by boiler steam [3], was not made by Foulk nor by other investigators of the foaming of boiler water.

Attempts to prevent the foaming of boiler water can follow three courses, corresponding to the three factors mentioned:

1) action on the colloid part of the foaming system by lowering the content of colloids, e.g., by a more complete extraction from the feed water of calcium and magnesium salts which give finely divided precipitates, by preventing the corrosion of iron in the boiler, or by changing the degree of dispersion of the colloid substance;

2) decreasing the concentration of electrolyte in the boiler water by blowdown;

3) diminishing the rate of fall of pressure, eliminating sharp fluctuations in the running of the boiler, smooth opening of the steam regulator.

The latter, third, means is utilized by the best locomotive engineers and allows them, even in districts with known poor water, to increase the time between flushes and to save fuel. Laboratory investigations of this factor were carried out by Fesenko.

Officially, both in electric power stations and in rail transport, the second method is used - blowdown of the boiler. The intensity of the blowdown is established experimentally, because present theory does not provide a sufficient criterion, and practice has shown that for each boiler it is necessary to establish its own 'critical load' above which, at the given salt content, a more intensive blowdown inevitably results in carrying salts away with the steam and even in the danger of ejection of water into the steam pipe. After a number of tests the salt concentrations which can ensure prolonged normal running of the boiler at the designed working pressure, are established.

The control of the blowdown is made relative to the total salt content (in power stations) or to the chloride content (on the railways).

A sharp change of established practical norms of salt content for different boilers, even those with the same system and same dimensions, is not explained. Thus, Shkrob [4] gives the following data.

In the condensate of the power station of the Shterovsk hydro-electric station the established norm for the dry residue of boiler water is 200 mg/liter, and for Zugres it is 1500 mg/liter. For a number of steam raising plants at the Urals Wagon Works the norm was found to be 1100 mg/liter and at Sevdongres, 4000 mg/liter. As a norm for boiler water of average pressure Shkrob [5] showed that, depending on the separatory equipment, a practical value of 1500-5000 mg/liter may be assumed.

Thus, such an important index of the running of a boiler as the percentage of blowdown water is only determined while the boiler is running. This percentage is also seriously affected by seasonal fluctuations in the feed water composition.

In rail transport things are more complicated, because the blowdown norms must be established separately for each 'Traction Branch' and for each type of locomotive. Any breaks in the chart showing the feed water composition at separate stations, indicating sharp changes in the quality of the water, can lead to unexpected foaming and foamy priming, or to scale formation.

For the further elucidation of the conditions of the formation of foaming systems in a boiler our work was extended in two directions relative to colloids and electrolytes. The investigation was made via the method of foamy priming [1][1].

Investigations by Nemirovsky [6] showed that foaming in a glass flask in the presence of an electrolyte is caused by inorganic colloids of negative charge. In an earlier investigation it was shown [1] that the foaming, conditioned by the presence of inorganic colloids of positive charge, is caused predominantly by the anions of the salt - by the sulfate, chromate, carbonate, chloride, etc., ions. Negatively charged colloids depend for their foaming action mainly on the cations: calcium, magnesium, sodium, potassium, barium, etc.

The values of the foamy prime are approximately the same for colloids of different sign. Thus, changing the sign (charge reversal) of the colloids cannot be of practical assistance in dealing with foaming.

In Nemirovsky's work (foaming in a glass flask - negative colloids) with a mixture of salts, considerable deviation from additivity in the direction of an enhanced foaming power was observed. Nemirovsky turned his attention to the fact that a larger foaming power is caused by negatively charged colloids of an intermediate degree of hydrophilic character. Strongly hydrophobic colloids, for example arsenic sulfides, do not cause foaming.

In the work of Fesenko [7] on mixing two and three electrolytes in an iron

[1]) Study of the foaming systems by the method of foamy priming is made by heating the solution under investigation (0.5 liter) in a flask (1 liter) after which the pressure on the solution is rapidly lowered (by 300 mm Hg in 10 sec). The intensity of the foaming is measured by the foamy priming, i.e. the number of ml of water carried away with the steam. The more stable the foam the larger the foamy prime, under the indicated conditions.

flask, non-additivity of the foaming action was also observed. As a rule the mixture is more active than the separate components. In Figure 1, taken from the data of Fesenko, diagrams of foamy priming for the ternary system NaCl-Na_2CO_3-NaOH are displayed at a total constant concentration of 50 to 60 mg-equiv./liter. Figure 2 gives the same results for the ternary system Na_2SO_4-Na_2CO_3-NaOH, likewise at 50 and 60 mg-equiv./liter.

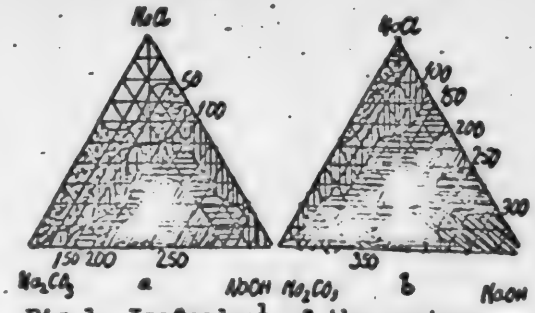

Fig.1. Isofrodes[1] of the system NaCl-Na_2CO_3-NaOH. Concentration of electrolytes (in mg-equiv/liter): a - 50; b - 60.

Figures on the diagram indicate the values of the foamy prime (in ml).

From the diagrams the strong foaming action of sodium sulfate relative to that of sodium chloride can be seen. In the first case a particularly strong action is produced by the ternary mixture corresponding, for example, to the center of the ternary diagram.

It should be borne in mind that, with different values of the total concentration of electrolytes, different distributions of the foamy prime on the diagram are produced. Fesenko obtained diagrams for total concentrations of 20, 40, 50, 60, 80, 100 and 120 mg-equiv./liter.

On the basis of Fesenko's data it can be calculated that for each concentration of mixture there is a unique value of the foamy prime. Plotting such calculations for a prime of 200 ml (from 500 ml solution in a liter flask, which corresponds to half the maximum prime) we obtained the diagrams displayed in Figures 3a and 3b.

The different character of the isoconcentration lines on going from sodium chloride to sodium sulfate can be seen at a glance. One and the same prime may be obtained at a total concentration changing from 44 to 74 mg-equiv./liter.

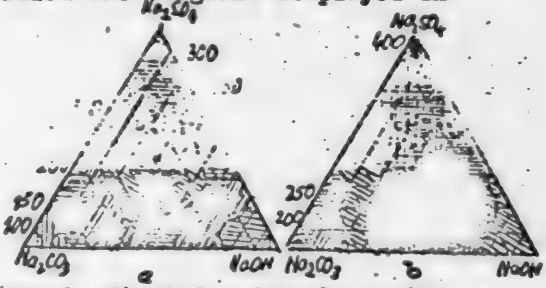

Fig.2. Isofrodes for the system Na_2SO_4-Na_2CO_3-NaOH. Concentration of electrolytes (in mg-equiv./liter): a - 50; b - 60.

Figures on the diagrams indicate values of foamy primes (in ml).

We met with very different foaming powers at one and the same total concentration. This showed that the value of the general salt content cannot serve as a basis for the standardization and control of blowdown. It is necessary to take into consideration that, at equal concentrations, chlorides have better electrical conductivities than sulfates. Consequently, measures of salt content, obtained by measurement of electrical conductivity, only weakly reflect an increase of sulfate concentration and in typical continental feed waters such as that of Donbass, N. Caucasus, Kazakhstan, etc., sulfate predominates over chloride. A mechanical, generalized approach to this question should be replaced by the establishment of the location of the boiler water composition on the foaming diagrams.

In the composition of boiler water it is necessary, for a first approxima-

[1]) Isofrode = line of constant foaming power.

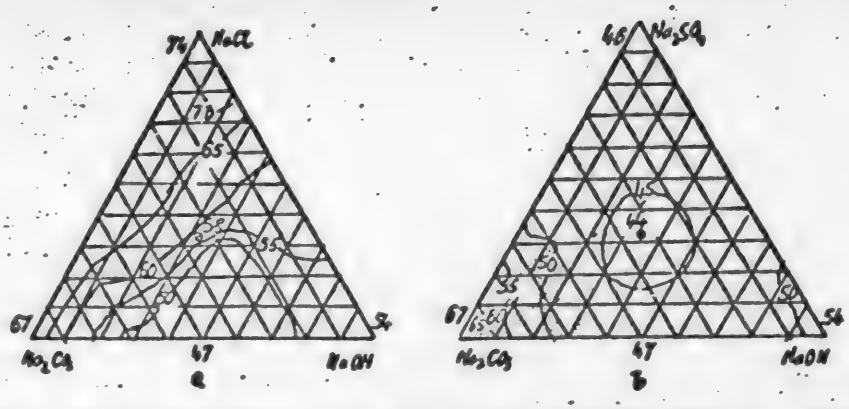

Fig.3. Isoconcentration lines for foamy prime π = 200 ml. Figures indicate total concentration, in mg-equiv./liter.

a - system NaCl-Na_2CO_3-NaOH; b - system Na_2SO_4-Na_2CO_3-NaOH.

tion, to take account of the sulfate and chloride content and also that of sodium carbonate and caustic soda. In high pressure boilers sodium carbonate has little importance. In power stations attention should be directed to the relationships between the three electrolytes: Na_2SO_4, NaCl, NaOH. On the railways the feed water must be characterized not only by its hardness and by a quantitative determination of the chloride (for calculation of the anti-scaling dose) but the alkalinity and chloride content should also be determined. We earlier showed the importance of sulfates for normal blowdown on rail transport [6].

The use of the so-called 'caustic soda number' is based on an annoying misunderstanding introduced into boiler practice by American investigators, and is not justified nowadays. It is necessary to take account of the content of each electrolyte, and the effect of their mixtures in the presence of inorganic colloids should be determined from diagrams.

Attention should be directed to the formation of slimy deposits of such a degree of dispersion and hydrophilic character as will inhibit, on the one hand, the formation of solid crystalline scale and, on the other hand, the formation of stable foamy systems.

We propose to extend our work further to a study of the effect of mixtures of colloids and of mixtures of electrolytes - more complex and with other ions.

At present we can already assert that the prevention of foamy priming of boiler water by the use of mechanical separators and blowdown is not so simple as appeared at first glance and is not economical in the majority of cases.

A solution of this question depends on the action of the colloidal part of the foaming system.

SUMMARY

1) In an investigation of the foaming power of boiling solutions, by the method of foamy prime it was found that mixed electrolytes as a rule, are more effective than would be expected from the additivity rule.

2) The foaming action of inorganic colloids of both positive and negative sign has been established.

3) Diagrams of foamy primes for ternary systems of electrolytes, characteristic of boiler water in iron boilers, have been obtained.

4) The method of controlling boiler blowdown by the chloride or total salt content of the boiler water, should be replaced by the more rational method of determining the foaming power from diagrams for ternary (and quaternary) systems.

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SECOND ALL-UNION CONFERENCE ON THE HISTORY OF RUSSIAN CHEMISTRY

The second All-Union Conference on the History of Russian Chemistry, held in Leningrad on April 21-26, 1951, provoked great interest and attracted many participants. More than 80 member chemists came from Erevan, Baku, Sverdlovsk, Kharkov, Riga, Kishinev, Yaroslavl, Kazan, Tomsk, and other towns.

The conference opened with some introductory remarks by M. M. Dubinin, the Academic Secretary of the Division of Chemical Science of the USSR Academy of Sciences who noted that, during the time which had elapsed between the first and second Conferences on the History of Russian Chemistry, important developments had taken place in the scientific life of our country, having an enormous effect on the further progressive development of Soviet science.

Acad. Dubinin said that the inspired work of Josif Vissarionovich Stalin in the field of linguistics constituted a new and powerful stimulus for developments in all fields of science. This work by J. V. Stalin had a special and great significance as a guide for the working out of a methodological basis for the history of chemistry.

Afterwards Acad. A. E. Arbuzov, the chairman of the Commission on the History of Chemistry, rose. He reviewed the whole work of the first Conference, in which was noted the fundamental value for physical chemistry of the outstanding work by the gifted representative of Russian science, Mikhail Vasiliev Lomonosov. It was proved at the first Conference on the History of Russian Chemistry that the opinion which had been held for decades - that W. Ostwald was the founder of physical chemistry - was incorrect. Ostwald was still a student at the Realschule in Riga when Acad. N. N. Beketov, in 1860, delivered to the students at Kharkov University a course entitled 'Relation of Physical and Chemical Phenomena to One Another', and in 1865 Beketov initiated a course on 'Physical Chemistry'. Enormous contributions to the development of physical chemistry were made by the outstanding Russian scientists D. P. Konovalov, V. F. Alekseev, N. S. Kurnakov, N. A. Menshutkin, I. A. Kablukov, V. F. Luginin, and many others.

Corresponding member of the USSR Academy of Sciences A. A. Maximov, in his report 'Significance of the Work of J. V. Stalin on Linguistics for the History of Natural Science' showed that the work of J. V. Stalin on linguistics constituted a new step in the development of Marxist theory and in the general advance of science.

Class ideology acts as the weapon of class interest in the theory of science Objective truth always enters into the composition of this or that view of the world, expressed in this or that ideological form. Bourgeois ideology, inimical to science, makes special use of one-sided, incomplete, and relative scientific knowledge.

Corresponding Member of the USSR Academy of Sciences, B. A. Arbuzov, in his report 'Butlerov's Theory of Structure and its Development' emphasized that the importance of this structural theory, one of the greatest achievements of human genius, had become particularly clear recently, when such basic concepts in chemistry as the nature of the chemical bond were under criticism and review, from the standpoint of dialectical materialism. The report showed that bourgeois chemical history usually belittles Butlerov as the author of structural theory,

and that the task of Soviet scientists is to combat all idealistic views, and to deepen and extend the theory of structure of organic compounds on the basis of the achievements of present-day science.

Acting Member of the Academy of Sciences of the Azerbaijan Federal Republic, Yu. G. Mamedaliev devoted his report to the 'History of the Development of Petroleum Chemistry in Russia'. The basis of the scientific chemistry of petroleum was laid, said the report, by the notable investigations of the outstanding exponents of Russian science - A. M. Butlerov, D. I. Mendeleev, N. D. Zelinsky, G. G. Gustavson, V. V. Markovnikov, M. I. Konovalov, and S. S. Nametkin, whose work, for those days, is astonishing for its deep creative sense, and for its gift of scientific prevision. By using Butlerov's reaction in hundreds of plants throughout the world, the needs of contemporary aviation for millions of tons of isooctane are satisfied. The talented Russian scientist Yu. V. Lermontova, a representative of the Butlerov school, achieved an extremely illuminating synthesis of isooctylene by alkylation of isobutylene with tertiary butyl iodide.

Butlerov's own evaluation of his discovery of the conversion of unsaturated hydrocarbons into the corresponding saturated alcohols, is an example of scientific prevision: 'The reaction promises to acquire practical value in time; should a cheap source of ethylene be discovered it would then provide a method for the manufacture of alcohol.' At the present time ethyl and other alcohols are synthesized on the large scale, the raw material being the unsaturated hydrocarbons present in the gas resulting from pyrolysis and cracking.

G. G. Gustavson was the first to indicate the catalytic properties of aluminum halides; he studied in detail the products of interaction of alkyl halides with aromatic hydrocarbons, and carried out a searching investigation to elucidate the mechanism of the reaction of organic compounds in the presence of aluminum halides. He was the first in the history of science to achieve the catalytic transformation of petroleum hydrocarbons in the presence of metal halides. The first-rate significance of G. G. Gustavson's investigations has been intentionally ignored by many foreign authors.

More than 20 years of productive work were devoted to the investigation of the composition of Caucasian petroleum by A. M. Butlerov's pupil, V. V. Markovnikov. The chemical method for the concentration of petroleum hydrocarbons, which Markovnikov worked out, is used in all the laboratories of the world.

The labors of Vreben, justly including those of Acad. N. M. Kizhner, constitute cornerstones of a wide section of organic chemistry, the cyclic hydrocarbons group, and have had a decisive effect on the treatment of petroleum.

M. I. Konovalov, a pupil of V. V. Markovnikov, enriched petroleum chemistry with the important reaction - the nitration of paraffins with dilute nitric acid.

The contribution of N. D. Zelinsky to the use of synthetic catalysts for the decomposition of petroleum and the treatment of its decomposition products, was illustrated by a series of historical examples. It was shown that the path followed by Russian science, from the first investigations of G. G. Gustavson to the works of N. D. Zelinsky, S. V. Lebedev, and S. S. Nametkin, led to the creation of the catalytic cracking industry as a result of world-wide activity in the field of petroleum refining.

Cand.Hist.Sci. N. M. Raskin, in his report 'Vasili Ivanovich Klementev-Student and Assistant of M. V. Lomonosov', described the character of the experimental work carried out in Lomonosov's laboratory, gave an account of some of

Lomonosov's first assistants, their training and round of duties, and also supplied some biographical details about V. I. Klementev. The report showed the importance of the latter's work, and the difference between his education and the usual training received by chemists in the middle years of the nineteenth century.

The initiators of the first Russian Chemical Journal, as Cand.Chem.Sci. Yu. S. Musabekov related in his report 'First Russian Chemical Journal and its Foundation', were the leading chemists and public figures N. I. Sokolov and A. I. Engelhardt. In two years 24 issues of the journal were published. The 'Russian Chemical Journal' first appeared in 1859, considerably before some well-known West-European and American chemical journals. The founders of the Chemical Journal gathered around themselves an outstanding collection of authors. N. N. Zinin, A. M. Butlerov, D. I. Mendeleev, N. N. Beketov, V. V. Markovnikov and others collaborated on the journal.

Cand. Pedagog.Sci. N. I. Chasovnikov dealt with 'Chemical Educational Literature in Russia in the 18th Century'. The teaching of general chemistry, and of testing skill, i.e. of analytical chemistry started in Russia in the seventies of the eighteenth century. From 1772 to 1801 15 editions of general chemical textbooks, covering 12 titles, were published. The most successful of these books, for which most editions were needed, was one which had a practical bias.

Cand.Chem.Sci. S. I. Kuzmenko, in his report 'The Textbook' Complete General Chemistry for Pupils and Teachers' " by F. Gize and V. S. Komlishinsky, described the contents of this advanced treatise, which was of the nature of a chemical encyclopedia, and which appeared in the first quarter of the nineteenth century. The publication facilitated the development of chemical science in Russia.

Corresponding Member of the USSR Academy of Sciences V. I. Spitsyn presented, in his own name and that of V. I. Baranov, a report entitled 'History of the Work on Radioactivity at Moscow University' in which he showed that the scientists at Moscow University made considerable contributions to the development, in Russia, of the investigation of radioactivity at the beginning of the present century, and that their research work had been closely connected with the training of scientific cadres in this field of chemistry.

Dr.Chem.Sci. O. E. Zvyagintsev, in his report 'Work of Acad. N. S. Kurnakov and His School in the Study of the Metals of the Platinum Group', discussed the outstanding work of N. S. Kurnakov in the field of platinum compounds, the use of physico-chemical analysis for the study of the complex platinum compounds and the importance of Kurnakov's work for the Soviet platinum industry.

Prof.A. K. Kolosov, in his report 'Development in Russia of the Manufacture of Nitric Acid by the Oxidation of Ammonia by I. I.Andreev's Method', described the state of the industry in Russia at the beginning of World War I, and the work of the Russian scientist I. I. Andreev who, showing himself to be a fervent patriot of his motherland under the difficult conditions of Tsarist Russia solved a considerable technical problem, and created the first Russian plant for the manufacture of contact nitric acid.

A unique competition was organized between I. I. Andreev's plans and those of an Anglo-Norwegian firm, in which the fertility of the technical conceptions of Russian chemists, and the backwardness of technical ideas among foreign chemists, was demonstrated. After the competition, I. I. Andreev was

offered the project of constructing his own contact apparatus by the representatives of the capitalist world: among other things the Russian Government allowed English enterprises and the French War Mission to acquaint themselves with designs and materials for, and details of, the production of nitric acid. Thus, Russia's allies undoubtedly utilized I. I. Andreev's method for the construction of their nitric acid plants. The reporter considered that the priority of Russian chemist I. I. Andreev in the creation of contact apparatus, and of catalysts from alloys of the platinum group metals for the oxidation of ammonia to nitric acid, was firmly based. However Andreev's work has been undeservedly forgotten, and all textbooks of general chemistry mention only Ostwald's method of obtaining nitric acid, and ignore Andreev's. But the investigations on the fixation of atmospheric nitrogen, which Andreev initiated, have not been laid aside, but are continuously being improved by our Soviet chemists.

Acad. M. M. Dubinin dwelt on 'Development of Antigas Measures in the Soviet Union'. The history of the development of antichemical defence in our country, he maintained, is a clear example of the outstanding role of Russian and Soviet scientists, engineers, and practical men in the creation of new technical fields, and of special divisions of chemistry. Professors, lecturers at the institutions for higher learning, and many chemists took an active part in the working out of antigas measures for the protection of armies from toxic substances. The report discussed the fact that in August 1915 N. D. Zelinsky made a communication concerning the absorptive capacity of charcoal, and in November of the same year a special commission tried out Zelinsky's antigas canister in conjunction with Kummant's masks.

Zelinsky's antigas material gained enormous popularity in the army and saved tens of thousands of lives. Prof. N.A Shilov advised the staff at the front and the staffs of the Allied armies on questions of antigas combat, and as a result appears to have been the essential initiator of the antigas service at the front. In mobile laboratories and in wagons, not only were tests carried out, but the beginnings of serious scientific investigations of the subject were made. In particular, the method of evaluating the quality of a carbon by measuring its dynamic activity was so developed.

Dr.Chem. Sci. N.A.Figurovsky, in a report entitled "Methodological Introduction to a Course on the History of Chemistry," reported the contents of a course on the methodological basis of the history of chemistry. He showed the value of the work of J.V.Stalin, relative to dialectical and historical materialism, for the investigation and study of the history of chemistry, dwelling on the fundamental tasks of the history of chemistry as a science. One of the most important tasks, he said, is the disclosure of the dialectical character of the development of chemistry in all periods of its history, and, for example, the dialectical character of the development of individual scientific problems. It is necessary to show the historical processes in their development more frequently, to show the struggle between materialism and idealism in chemistry during its historical development to demonstrate the importance of the history of chemistry, and of the study of practical work by preceding generations for the understanding of contemporary processes and phenomena in the development of chemistry and for getting further perspectives in science. The lecturer dwelt further on the problem of breaking up the history of chemistry into periods, on the connections between the history of chemistry and general history and the history of philosophy, and on the work of J.V.Stalin in linguistics and its significance for the correct solution of the problem of breaking up the history of chemistry into periods. He

emphasized the significance of discoveries by our own chemists for combatting servility and obsequiousness towards Western science and its representatives.

Prof. B.M.Kedrov, in his report "The Course of the Development by D.I. Mendeleev of the Periodic Classification of the Elements," attempted to trace, by a study of the early variants of the periodic system, the development of Mendeleev's ideas during the creation of the periodic system of the elements, and the discovery of the periodic law.

Docent A.Kh.Arutyunyan, in his report "General Features of Applied Chemical Knowledge in the Middle Ages in Armenia and Ancient Russia," showed that the first literature information about contact between Armenians and Russians dates to the tenth century according to Armenian sources, and to the eleventh and twelfth centuries according to Russian sources. The numerous relics of material culture, and the similarity of the mythologies in Russian and Armenia, bear witness to the fact that this contact already existed at very remote times. The period of greatest development of applied chemical knowledge in Armenia coincided with the flowering of feudalism, the development and growth of towns and of artisan production, and with the emergence of the new class of the mercantile bourgeoisie. This period was the epoch of the rise and development of applied and rational knowledge in Armenia.

Study and comparison of the prescriptions of Russian and Armenian masters in the Middle Ages shows them to be characterized in particular by a similarity of exposition, of methods of expressing gravimetric relationships, and of concreteness and brevity of language. Apparently, during the eleventh and twelfth centurues, the Russian and Caucasian countries still exchanged their rich experience in this field. Recipes for pigments with which works of art were painted were known a long time ago to Russian Masters, but have reached us only in the writing of the 17th and 18th centuries, because these recipes were lost in the Tartar invasion.

There is no doubt that all this complex applied chemical knowledge, which bourgeois historians have ascribed to a definite circle of "select" countries, existed in Russia and a number of neighbouring countries which are now parts of the Soviet Union.

Cand. Tech. Sci. B.V.Nesmelov spoke on "Russian Scientists, Founders of Current Methods of Industrial Hydrogenation." He said that Russian scientists had played an outstanding role in the application of modern methods of industrial hydrogenation. The method for the direct introduction of hydrogen into organic compounds was worked out in 1861 by N.N.Zinin. The first experiments on the catalytic hydrogenation of a large number of organic compounds were made by M.M.Zaitsev, a pupil of the Kazan school, with the idea of hydrogenating fats. With the achievement of the hydrogenation of fats abroad, the experiments of a small Russian factory gained wide use.

Prof.Lukyanov read a paper on "History of the Discovery of Chromium and of the Production of its Compounds in Russia." The history of the discovery of chromium is closely connected with Russia. The Russian Academician Leman found, in the Urals in 1766, a rock containing chromium. In 1798 a mineral was found on the banks of the River Vyasgi in Siberia in which Tovy Lovits also found chromium. Crocoite (a chromium-containing mineral) was investigated by the greatest analysts of those times) Vauquelin and others.

The history of the development of the production of chromium salts in Russia starts in 1811, when a porcelain vessel colored by chromium oxide was first brought from Paris. The speaker further dwelt on the organisation and

technology of the production of chromium salts in the 19th century, according to information given by Prof. S.Dvigubsky (1828), Ilenkov (1851), Mendeleev (1871), Khodnyaeva (1855), and Krupsky (1873); at the end of his report Prof. Lukyanov mentioned the health aspect of the production of chromium, according to information given by Prof.Ge (1882).

Prof. N.A.Toropov gave a paper on "Work of Russian Scientists in the Synthesis of Silicates." He said that the work of our own scientists took a leading position in the first steps that were taken in this field of science. Pride of place should be given to K.D.Khrushchev who first obtained synthetic hornblende. At the beginning of the 20th century, the period of vigorous development of silicate chemistry in our country opened. Yu.F.Levinson-Lessing began systematic work on synthetic silicates. V.I.Vernadsky and P.A.Zamyatchensky carried out remarkable work on aluminosilicates. After the Great October Socialist Revolution, the synthesis of silicates was pursued on a larger scale, and experimental centers were created for the development of work on silicates.

Cand. Chem. Sci. F.M.Perelman, in his own name and that of Cand. Chem. Sci. A.Ya.Zvorykin, presented a report on "The Part Played by D.I.Mendeleev in the History of the Discovery of the Rare Earth Elements." He said that the discovery of each chemical element involved many links and was the work of many investigators.

Foreign scientists oversimplify this question and belittle the importance of Russian scientists in this field. In 1873 Mendeleev established that the double nitrates of the cerium earths with ammonium have different solubilities. By fractional crystallization, lanthanous salts are concentrated in the precipitate, and a salt of "didymium" remains in solution. E.Brauner a friend of Mendeleev, soon discovered, by optical means, two elements in " didymium", α- and β- " didymium."

In 1885 Auer von Welsbach repeated D.I.Mendeleev's experiments and noted that part of the "didymium" separated in the precipitate along with lanthanum. However, passing over in silence the work of Mendeleev (and of Brauner), and the decomposition of "didymium" into two new elements ("praseo-" and "neo-didymium"), he took all the credit himself. Meanwhile it is incontestable that the work of Mendeleev played a large part in the investigation of the lanthanum earths, and was closely connected with four elements of this group: scandium, lutecium, neodymium, and praseodymium.

Acad. S.I.Volfkovich spoke on "The History of Russian Production of Phosphate Fertilizers." He said that the basis for the use of phosphorites in the compounding of organic fertilizers was laid several hundred years ago, by the discovery of elementary phosphorus in 1659. Organized work on the use of fertilizers in Russia started in the middle of the 18th century. The lecturer said that our native artificial phosphate fertilizer industry was started in the second half of the nineteenth century. The noteworthy investigations of A.N.Engelhardt and of A.S. Ermolov on phosphates, and the beginning of planned work on fertilizers, were based on the labors of D.I.Mendeleev. At the end of the 19th century, only factories for the treatment of bones were comparatively widely distributed in Russia. At that time there were 13 factories for making superphosphate. In 1917 a public committee was organized to deal with fertilizers, and after two years a scientific fertilizer institute was opened as a result of its activities.

In 1928-1930, as a result of geological investigations by the USSR Academy of Sciences, under the leadership of S.M.Kirov, the great Khibin mining-chemical combine was set up.

Reports by Acad. A.E.Arbuzov (Kazan), Corresponding Member of the USSR Academy of Sciences S.N.Danilov (Leningrad), Corresponding Member of the USSR Academy

of Sciences A.D.Petrov (Moscow), Corresponding Member of the USSR Academy of Sciences B.A.Arbuzov (Kazan), Prof. V.I.Esafov (Sverdlovsk), Prof. M.P.Orlova (Tomsk), Prof. E.E.Martinson (Leningrad), Dr. Chem. Sci. A.F.Plat (Moscow), Dr.Chem.Sci. F.Shostakovsky (Moscow), Docent P.I.Protsenko (Rostov-on-Don), A.Kh.Batalin (Chkalov district), Cand. Chem.Sci. S.N.Kuzmenko (Kharkov), M.I. Batuev (Moscow), Sci. Collab. T.S.Kudryatsev were heard by the plenary, intersectional, and sectional sessions of the Second All-Union Conference.

Closing the Second Conference on the History of Russian Chemistry. Acad. A.E.Arbuzov remarked that an overwhelming majority of young scientific workers had participated in the work of the conference both by presenting reports and speaking in the discussions; many of them had with enthusiasm become acquanted, through primary sources, with the history of the development, in our country, of separate trends both in theoretical science, and in the manifold applications of science in industry.

He said that historical science relative to the development of natural science in our country particularly the history of the development of chemistry, was still young, which was not at all surprising, as young cadres of historians of chemistry have only been trained in recent years.

Summing up the work of the conference, Acad. A.E.Arbuzov stated 124 reports by 102 authors had been presented to the audience; the Commission on the History of Chemistry had dealt with 65 reports, including 37 in the announcement of the conference, of which 34 were heard. 18 more reports were dealt with outside the working time of the conference, and it was naturally not possible to hear them.

At the end of his speech he expressed confidence that the participants in the Second All-Union Conference on the History of Russion Chemistry had considerably enriched their knowledge of the development of chemical science in our country, and wished all the participants further success in the noble work of demonstrating the greatness and significance of Russian chemical science.

In the decisions of the Conference it was noted that there had been a considerable development of investigation and re-examination of the history of Russian Chemistry. The number of published works and communications on the history of Chemistry continued to grow. The "Journal of Applied Chemistry" and some others, for example "Progress in Chemistry" regularly published communications on the history of chemistry; the number of authors of papers and notes on this subject had increased. In the past the Commission on the History of Chemistry had undertaken publishing activity. It had brought to light the selected works of A.M.Butlerov, the first volume of the complete works of M.V. Lomonosov and other publications on the history of Russian Chemistry.

However, in spite of all these achievements, the Conference was not able to consider the state of work on the history of chemistry as satisfactory, and it noted the following important deficiencies in the organization and carrying out of work on the history of chemistry.

1) Much too slow development of the treatment of the methodolcgical bases of the history of chemistry. Discussions and consideration of materials were still not important parts of the work and technique of historians of chemistry. Up to the present time criticism and self-criticism were still very weakly developed in the investigation of, and in literary works on, the history of chemistry.

2) Not nearly enough of the investigation and work on the history of chemistry was devoted to the history of the development of Soviet chemistry.

Propaganda about the devlopment and achievements of Soviet chemistry was quite small, and was frequently devoted not to central questions of the development of chemical science, but to individual fields and to secondary questions.

3) In their printed contributions, a considerable proportion of authors of papers on the history of chemistry, not infrequently presented bare factual material, without any attempt at a Marxist analysis of the historical events examined, or of the historical development of separate fields of chemical science in a definite period.

4) Many authors of papers on the history of chemistry, including qualified ones, not infrequently become confused in the ordinary literature compilation; they do not make use of original sources and archives, and they substitute such a compilation for a thorough and really profound approach to the proper scientific illumination of this or that problem of chemical history.

5) The Conference noted unsatisfactory work on the preparation for publication of scientific biographies of the classical Russian chemists, and of their selected works. Up to the present time no scientific biographies of Mendeleev, Butlerov, Zinin, Kurnakov, Favorsky, and other great Russian scientists have been prepared for publication. In the series, "Classics of Science," nothing has so far been published on the theory of solutions or on organic chemistry, etc., similar to "The Periodic Law" of D.I.Mendeleev.

6) Treatment of scientific archives and the publication of the unpublished works of our own classical scientists is extremely slow. Printed autobiographical and epistolatory material of individual scientists is dispersed through many publications, which makes the study and generalization of this material difficult.

7) The preparation for publication of a monograph on the history of Russian chemistry, to be included among the many volumes of the "History of Science and Technology in the USSR from Ancient Times to the Present Day" is also much too slow.

8) The output of cadres of young historians of chemistry is not sufficient. There are places for aspirants only at Moscow University, and there are no doctorates either in the Institute of the History of Natural Science, nor on the Commission for the History of Chemistry. As yet there is no textbook on the history of chemistry.

9) There is still little propaganda about the history of Russian chemistry and about the priority of discoveries by Russian chemists. The Society for the Dissemination of Scientific and Political Knowledge, and other organizations, rarely organize lectures on themes from the history of Russian chemistry.

The Conference resolved:

1) To consider as important tasks for the further work on the history of Russian chemistry:

a) the creation of a journal of the history of Russian chemistry on the lines of a prospectus worked out by the Editorial Board of the Division of Chemical Science of the USSR Academy of Sciences; b) production of a textbook on the history of chemistry; c) continuous strengthening and extension of research on the elucidation of the priority of Russian scientists relative to important scientific and technical discoveries and inventions, in chemistry and chemical technology; d) writing of biographies of classical Russian chemists; e) collaboration in the preparation for publication, by the Commissions, of works of classical Russian chemists and publication of separate works on chemistry by the Commission on the History of Chemistry; f) further scientific

treatment of archives relative to the lives and activities of Russian and Soviet chemists, printing material from the newly discovered documents in the publications of the Commission on the History of Chemistry and in chemical journals; g) and treatment of the history of chemistry in the Soviet period.

2) The Conference thinks it necessary to ask the Bureau of the Division of Chemical Science of the USSR Academy of Sciences, and the Commission for the History of Chemistry to organize, in the near future discussions on important questions concerned with the development of investigations on the history of chemistry, and with related tasks facing Soviet historians of chemistry. The most important problem, requiring considerable discussion, is that of starting a course on the history of chemistry in connection with the inspired work of J.V.Stalin in the field of linguistics.

3) The Conference had specially emphasized the need for many-sided improvements of instruction in the history of chemistry in universities and institutes of chemical technology, for the creation of obligatory sections of faculty courses, devoted to the history of chemistry, for the establishment of aspirantorates, and for the need to interest the student body in the treatment of various questions connected with the study of the activity of our own chemists, and with the development of chemical knowledge in our country. The Conference requests the Bureau of the Division of Chemical Science of the USSR Academy of Sciences to look into the question of establishing doctorates in the history of chemistry, in the basic chemical institutes of the Division.

4) The Conference considers it extremely desirable to have regular publication of the proceedings of the Commission on the History of Chemistry, and of reports and communications made at the sessions of the Commission and its branches, as well as those of separate investigators. The Conference requests the Bureau of the Division of Chemical Science of the USSR Academy of Sciences to give all necessary help and support to the Commission in this matter.

5) The Conference considers it necessary to disseminate, much more widely, spoken and written propaganda on the history of Russian chemistry, and urges the Society for the Dissemination of Scientific and Political Knowledge to produce and publish regularly reports concerning the history of Russian chemistry, and the priorities and achievements of Russian scientists and chemical engineers. The Conference considers it particularly important to deliver such papers in the regional and district centers of our country, in high schools, schools, plants and factories, collective farms, etc.

6) The Conference directs the attention of the Ministry of Higher Education of the USSR and the leading chemical research institutes to the need for careful preservation of relics of our great chemists, and recommends the creation of museums in universities for the collection of apparatus, samples, manuscripts, photographs, etc., of scientific and historical value, and necessary for the development of the history of chemistry.

7) The Conference considers it necessary for more work to be devoted to the bibliography of chemical literature, and to the preparation by the library of the USSR Academy of Sciences of the successive issues of the bibliography "Chemistry in the Publications of the USSR Academy of Sciences" which should be brought up to date.

The Conference calls upon all chemists, interested in the history of chemistry, to study untiringly the classical works of Marxism-Leninism, to extend their knowledge in the field of the history of Russian chemistry, and to expose decisively, by profound research, and by the extraction of unpublished archives,

the mendacious and falsified assertions of bourgeois historians of science - agents of monopoly capitalism - aimed at belittling the achievements of our Soviet chemists, and at spreading calumnies about our great country and its scientists. The struggle with reactionary and mendacious theories, and with the propaganda of bourgeois historians of chemistry, is the most important task for all Soviet chemical historians, who should, by their work, restore historical truth and evoke pride in our great Russian country.

P.M.Evteeva.

BOOK REVIEW

R.L.Pevzner

"THERMITE REFRACTORIES."

(Technical Press, 1951. 58 Pages. Price: 2r 30k.)

High alumina refractories have recently attained wide applications in many branches of the national economy. Besides the generally-known technique of producing these refractories by ordinary ceramic methods, i.e., by firing, their production by electrical fusion is also being put into practice in the USSR and in other countries. Production of electrically-fused mullite refractories in the USSR was started ten years ago at the Erevan plant. The creation of our own means of producing electrically-fused mullite refractories was a considerable achievement by our industry and at a certain stage it proved a great advantage to the glass industry. However, at this particular stage the electrical fusion of mullite did not meet the growing demand of the glass industry. This fact is mentioned in their book by the authors of the indigenous method for the production of electrically-fused mullite.[1] The extensive investigations of many authors have shown that corundum refractories have every advantage over mullite ones. At the same time the many difficulties of manufacturing corundum refractories by electrical fusion are known.

Prof. R.L.Pevsner's survey is devoted to a description of a new, indigenous, method for producing corundum refractories by the "Non-furnace Thermite Method". The appearnce of such a work is very timely.

In contrast to the generally-known methods, the new method of obtaining corundum refractories requires neither the use of furnaces nor the consumption of fuel or of electrical energy.

This basically new departure in the technology of the production of refractories is based on a complex combination of separate processes which only ensures a satisfactory technology called by the author thermite, when these processes are performed in a definite sequence.

The new technology worked out by Prof.R.L.Pevsner is based on the principle for the production of strongly reducing metals, first discovered by Acad.N.N. Beketov as early as 1865. This principle is based on the fact that aluminum, having a large affinity for oxygen, within known limits and at corresponding temperatures can be used as a reducing agent for the oxides of a large number of elements which have a smaller affinity for oxygen. The technological process for the production of thermite refractories consists in the separate preparation of the component of the charge, the fusion of the charge in a melting pan without special consumption of fuel or electrical energy, pouring of the high alumina melt thus obtained into special moulds, and the subsequent thermal treatment of the finished article. A large excess of heat is liberated in the whole process (40% above theoretical requirement); the melting of the charge takes only 2-3 minutes.

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[1]) See the book "Electrically-Fused Mullite Refractories for Glass-making." by A.A.Litvakovsky and M.V.Osipov (Technical Press 1950).

Comparison of the stability of electrically-fused mullite with that of thermite corundum under production conditions indicates that the latter product has a very high stability. Under the same severe conditions the thermite product appears to be 4 times as stable as the electrically-fused mullite refractory. All this is dealt with extremely briefly but circumstantially in this survey by the author of the new method. The works consists of a description of the technique the results of qualtity testing, and also gives the technical specifications for the evaluation of the qualtity of thermite refractories, which are already familiar and in production in some plants.

The following deficiencies in the book should be mentioned:-

1) Absence of data about the petrographic examination of the thermite refractories before and after service.

2) Extremely short description of the efficacity of thermite refractories. The author gives examples only for the glass industry, whereas there are grounds for supposing that they can find application in metallurgy and other fields. However, these deficiencies do not lower the general interest of this survey, and it can easily be extended to cover these fields in subsequent editions. The book is written extremely clearly, the illustrations are well drawn, and give a clear idea of the apparatus and of all the capabilities of this new and promising technology.

P.P.Budnikov.